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Supporting Information

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Parallel and Antiparallel Triple Helices of Naphthyridine Oligoamides**

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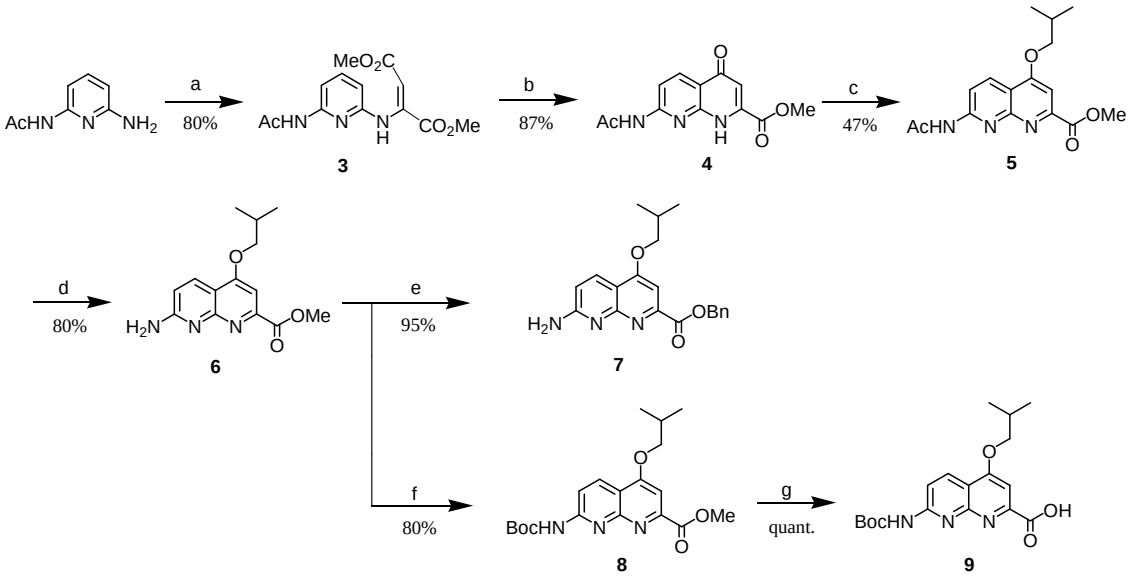
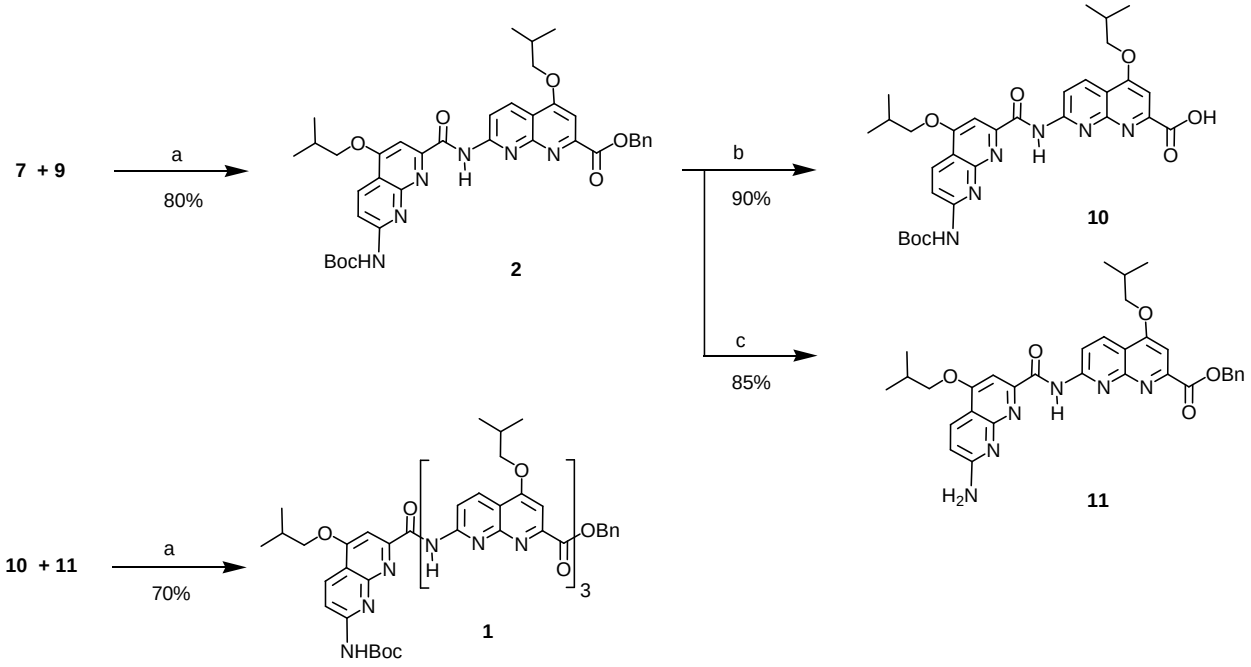
Synthetic schemes



Scheme S1. Synthesis of 1,8-naphthyridine-2-amino-5-isobutoxy-7-benzylester **7** and 1,8-naphthyridine-2-*N*-*tert*-butyloxycarbamate-5-isobutoxy-7-carboxylic acid **9**: a) dimethylacetylene dicarboxylate, MeOH, Δ; b) diphenyl ether, reflux; c) *i*BuOH, DIAD, PPh_3, THF, rt; d) H_2SO_4, MeOH, rt; e) $PhCH_2OH$, Et_3N, 60°C; f) di-*tert*-butyl dicarbonate, dioxane, Δ; g) NaOH, dioxane/water.



Scheme S2. Synthesis of tetramer **1** a) PyBOP, DIEA, $CHCl_3$, rt. b) H_2, Pd/C, DMF. c) TFA, CH_2Cl_2.

NMR solution studies

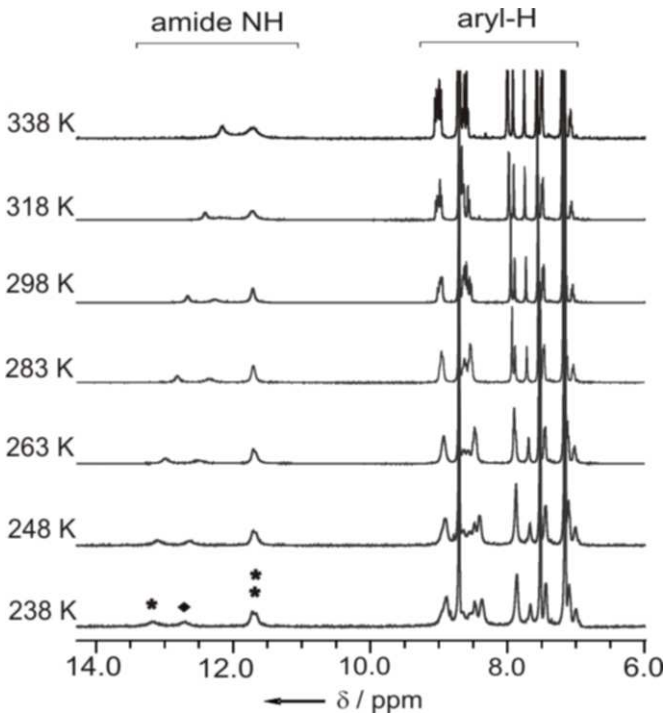


Figure S1. Variable temperature ^{1}H NMR spectra (400 MHz) of tetramer **1** (15 mM) in [D_5] pyridine. Stars represent amide signals and diamond represents terminal N*H tert*-butyl carbamate.

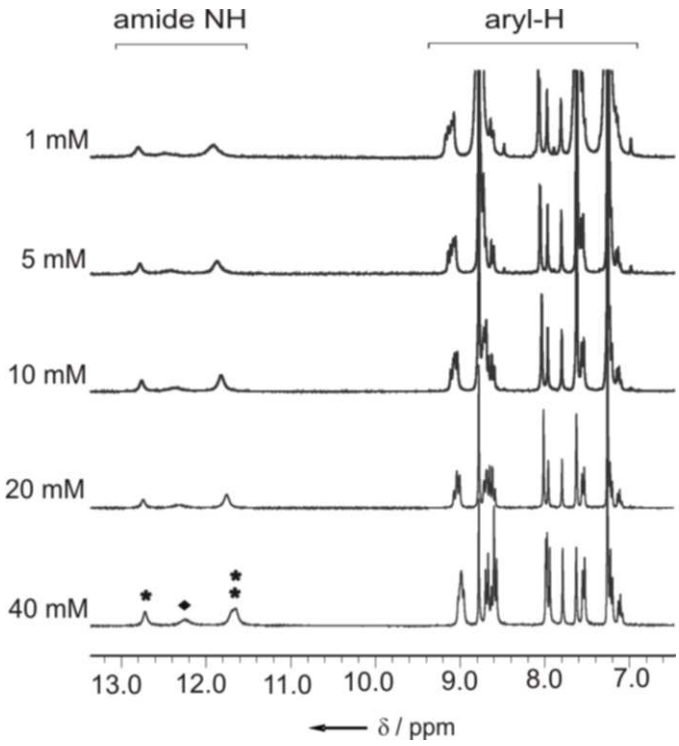


Figure S2. Part of 300MHz ^{1}H NMR of tetramer **1** at various concentrations in [D_5] pyridine at 298K. Stars represent amide signals and diamond represents terminal N*H tert*-butyl carbamate.

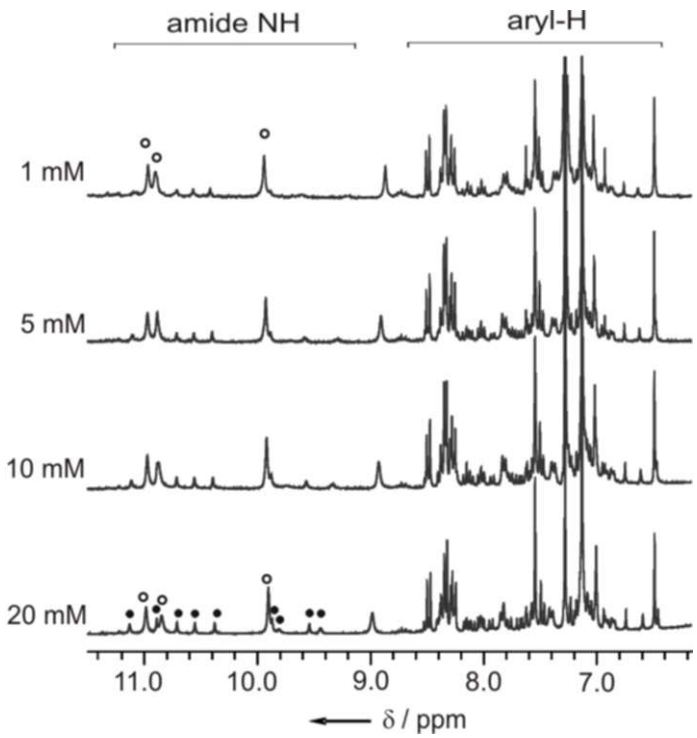


Figure S3. Part of 300MHz ^{1}H NMR of tetramer **1** at various concentrations in $CDCl_3$ at 298K. Empty circles indicate triplex in parallel configuration and black circles indicate the anti parallel configuration.

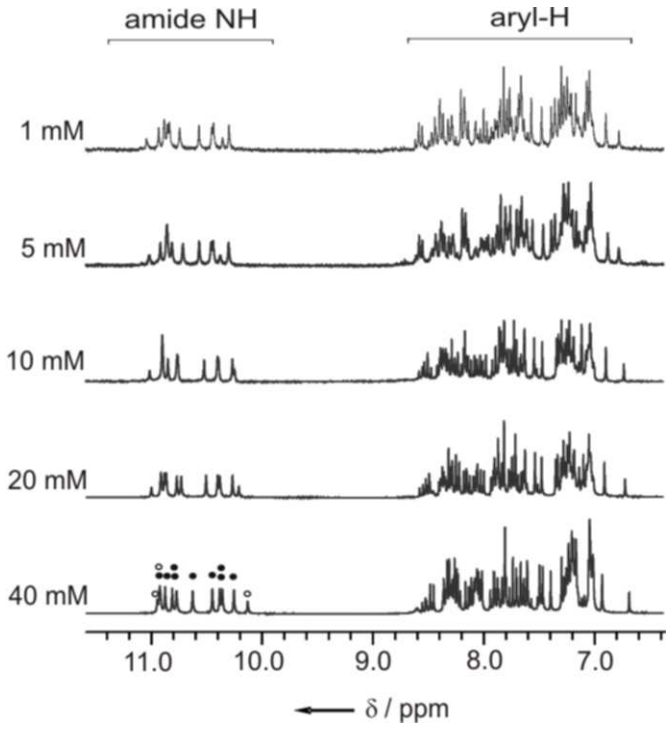


Figure S4. Part of 300MHz ^{1}H NMR of tetramer **1** at various concentrations in CD_3CN at 298K. Empty circles indicate triplex in parallel configuration and black circles indicate the anti parallel configuration.

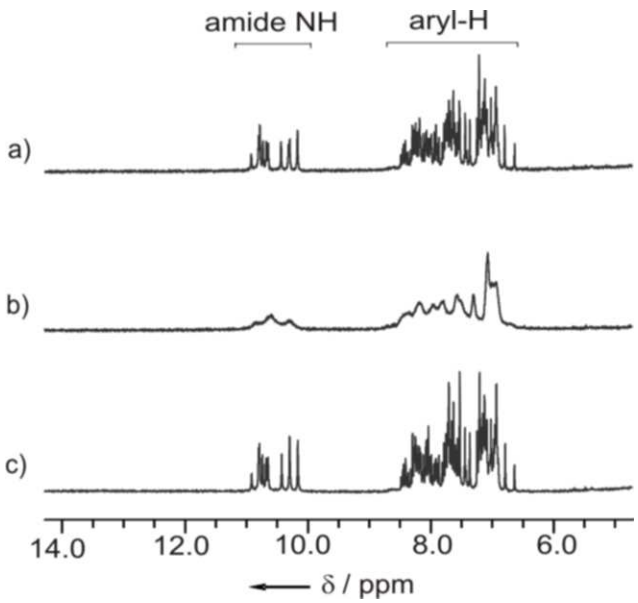


Figure S5. Variable temperature ^{1}H NMR spectra (300 MHz) of tetramer **1** (10 mM) in CD_3CN. a) spectrum recorded at 298K; b) spectrum recorded at 333K; c) after cooling back at 298K.

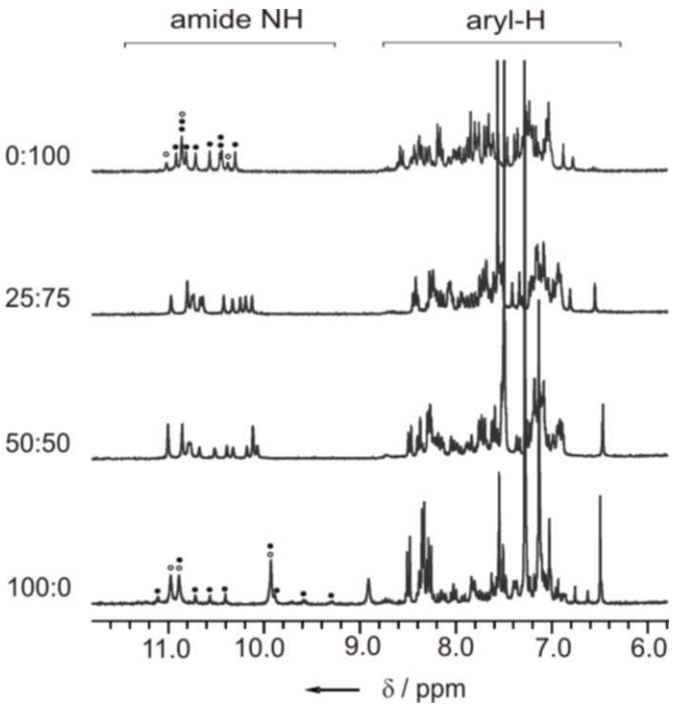


Figure S6. ^{1}H NMR spectra recorded at 298K (300 MHz) of tetramer **1** (4 mM) with different ratio of $CDCl_3/CD_3CN$.

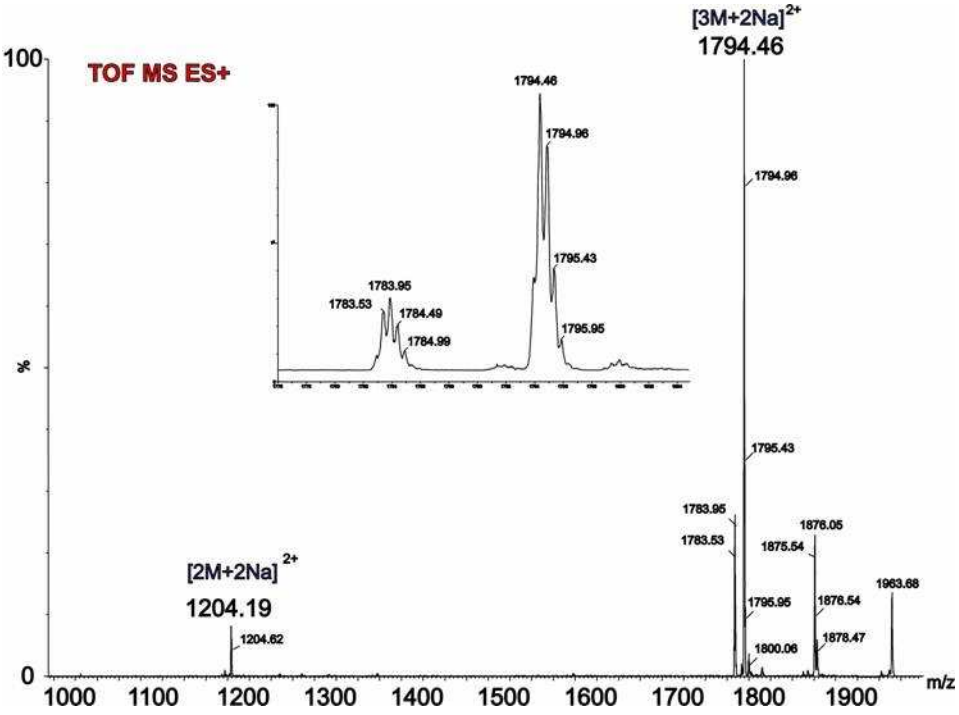


Figure S7. Electrospray mass spectrum of tetramer **1**

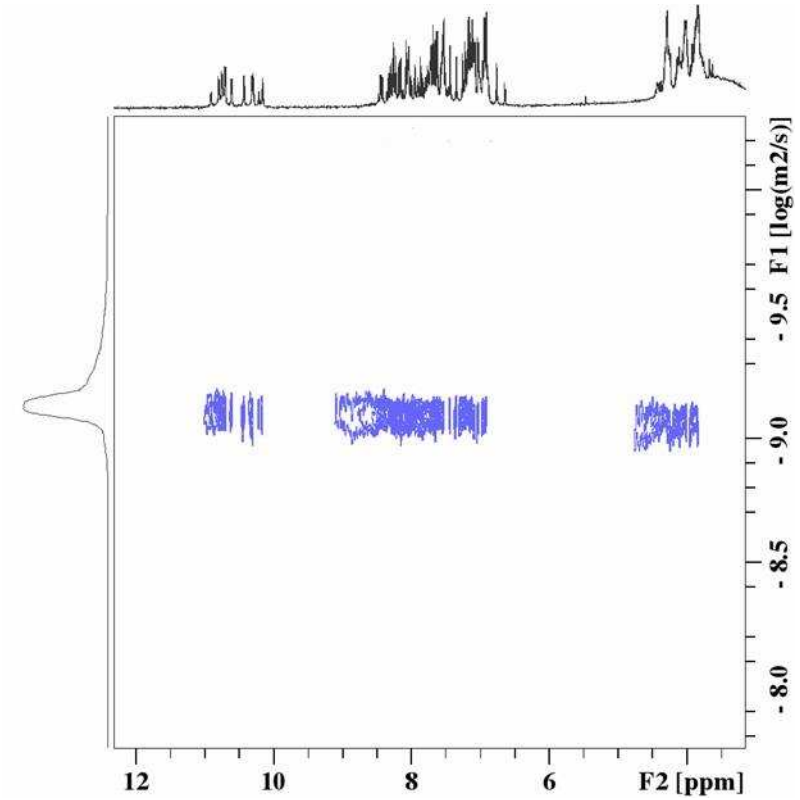


Figure S8. ^{1}H DOSY NMR spectra (300 MHz) of tetramer **1** at 298K in CD_3CN.

Crystallography

- Crystal structure of **1** as a single helix (CCDC # 754555)

Suitable crystals for diffraction experiments of compound **1** [$C_{64}H_{68}N_{12}O_{11}$] as a single helix were obtained by diffusion method from a pyridine/hexane mixture. Crystals belong to the monoclinic C2/c space group with unit cell parameters: a = 56.188(4) Å; b = 32.674(2) Å; c= 18.8225(11) Å; β = 100.339(3)°. Mr = 2979.28, V = 33995(4) $Å^3$, ρcalc= 1.164 $g.cm^{-3}$, Z = 8, μ = 0.658 mm^{-1}, no absorption correction, Ω scans, 161415 reflections collected, θ_{max} = 46.09°, 14373 independent with I > 2σ(I) (R_{int} = 0.098).
Refinement statistics: 1914 parameters, no restraints, Goodness-of-fit on F^2 = 1.534. Final R indices [I > 2σ(I)], R1 = 0.1393, wR2 = 0.3728, R indices (all data) R1 = 0.1854, wR2 = 0.3983.

- Crystal structure of $(\mathbf{1})_3$ as a parallel triple helix (CCDC # 754557)

Suitable crystals for diffraction experiments of compound $(\mathbf{1})_3$ [$C_{64}H_{68}N_{12}O_{11}$] as a parallel triple helix were obtained by diffusion method from a chloroform/pyridine/hexane mixture. Crystals belong to the trigonal R-3 space group with unit cell parameters: a = b = 34.405(5) Å; c = 37.395(8) Å; α = β = 90°; γ = 120°. Mr = 5230.80, V = 38333(11) $Å^3$, ρcalc= 1.360 $g.cm^{-3}$, Z = 6, μ = 2.305 mm^{-1}, no absorption correction, Ω scans, 11935 reflections collected, θ_{max}= 47.23°, 6709 independent with I > 2σ(I) (R_{int} = 0.075).
Refinement statistics: 1043 parameters, 42 restraints, Goodness-of-fit on F^2 = 1.964, Final R indices [I > 2σ(I)], R1 = 0.1953, wR2 = 0.4318, R indices (all data) R1 = 0.2059, wR2 = 0.4524.

- Crystal structure of $(\mathbf{1})_3$ as a antiparallel triple helix (CCDC # 754556)

Suitable crystals for diffraction experiments of compound $(\mathbf{1})_3$ [$C_{64}H_{68}N_{12}O_{11}$] as an antiparallel triple helix were obtained by diffusion method from chloroform/pyridine/hexane mixture. Crystals belong to the monoclinic C2/c space group with unit cell parameters a = 34.980(7) Å; b = 34.877(7) Å; c = 47.045(9) Å; β = 98.58(9)°. Mr = 4180.59, V = 56753(20) $Å^3$, ρcalc= 0.979 $g.cm^{-3}$, Z = 8, μ = 1.170 mm^{-1}, no absorption correction, Ω scans, 131018 reflections collected, θ_{max} = 44.51°, 22243 independent with I > 2σ(I) (R_{int} = 0.128).
Refinement statistics: 2582 parameters, 62 restraints, Goodness-of-fit on F^2 = 1.152, Final R indices [I > 2σ(I)], R1 = 0.1438, wR2 = 0.3525, R indices (all data) R1 = 0.2091, wR2 = 0.3893.

The three structures were solved by direct methods using the SHELXD program (Sheldrick, 2008),[1] and refined using the SHELX-L97 program (Sheldrick, 2008). Full-matrix least-squares refinement was performed on F^2 for all unique reflections, minimizing $w(F_o^2 - F_c^2)^2$, with anisotropic displacement parameters for non-hydrogen atoms. The positions of hydrogen atoms were located on a subsequent differential electron-density map. Hydrogen atoms were mostly spotted in Fourier differences but included in

idealized positions and refined with a riding model, with Uiso constrained to 1.2 Ueq value of the parent atom (1.5 Ueq when CH_3). The positions and isotropic displacement parameters of the remaining hydrogen atoms were refined freely.

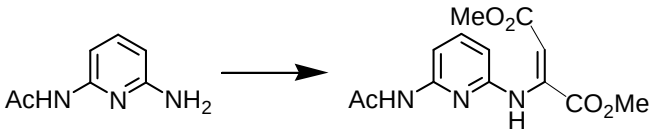
Squeeze from the Platon suite[2] was used to cure for the disordered solvent syndrome in crystal structure refinement of both parallel and antiparallel triple helix. Despite this treatment statistics are modest but acceptable for such big cells with high disordered solvent content.

Table S1. Twist angles between for each adjacent naphthyridine ring measured in the parallel and antiparallel triplex crystal structures. [3]

	$(1)_3$ parallel	$(1)_3$ anti-parallel		
		1st strand (head-to-head)	2nd strand (head-to-head)	3rd strand (head-to-tail)
N1-N2	27.36°	27.80°	27.75°	30.51°
N2-N3	25.72°	27.14°	27.14°	20.68°
N3-N4	27.10°	24.13°	24.13°	32.91°

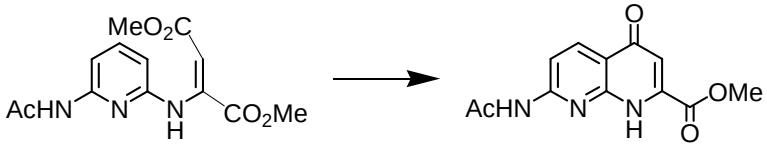
Experimental section.

General. All reactions were carried out under a dry nitrogen or argon atmosphere. Unless otherwise noted, the original materials were used directly from commercial supplies without any purification. THF was dried over alumina column, dry dichloromethane, chloroform, disopropylethylamine and triethylamine were distilled from CaH_2 prior to use. NMR spectra were recorded on Bruker DMX 300 and Bruker AVANCE 400 spectrometers. Chemical shifts are expressed in parts per million (ppm, δ) using residual solvent protons as internal standards (chloroform: δ 7.26 ppm; DMSO: δ 2.50 ppm; [D_5] pyridine: δ 8.78 ppm; CD_3CN: δ 1.96 ppm). Coupling constants are expressed in Hertz. EI, ESI mass spectra and MALDI-TOF were obtained on GCT, LC-MS 2010, and Autoflex spectrometers, respectively.



3

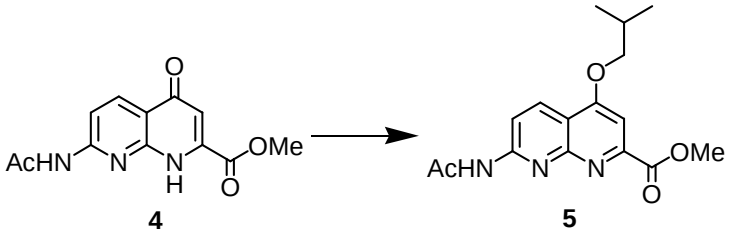
To a solution of N-(6-Aminopyridin-2-yl)acetamide[4] (284 mmol, 43 g) in 350 mL of methanol was added an equimolar amount of dimethylacetylene dicarboxylate (284 mmol, 35 mL). The resulting mixture was heated at reflux for 8 h. The solution was then cooled and the solvent was evaporated up to ca. 100 mL. The flask is then placed at -18°C for 4 h for precipitation. The resulting yellow prisms were collected by filtration, and washed several times with cold methanol (ca. 100 mL at -18°C) and dried under reduced pressure to yield 67 g (80 %) of fumarate derivative **3**. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm = 9.91 (br s, 1H); 7.78 (d, ^{3}J = 7.8 Hz, 1H); 7.60 (t, ^{3}J = 7.8 Hz, 1H); 7.53 (br s, 1H); 6.55 (d, ^{3}J = 7.8 Hz, 1H); 3.75 (s, 3H); 3.74 (s, 3H); 2.17 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm = 169.3; 168.6; 165.5; 150.4; 149.4; 145.9; 140.4; 107.5; 107.2; 96.3; 52.6; 51.4; 24.6. HRMS (ES^+): *m/z* calcd for $C_{13}H_{15}N_3O_5Na$ $[M+Na]^+$: 316.0909 found 316.0913.



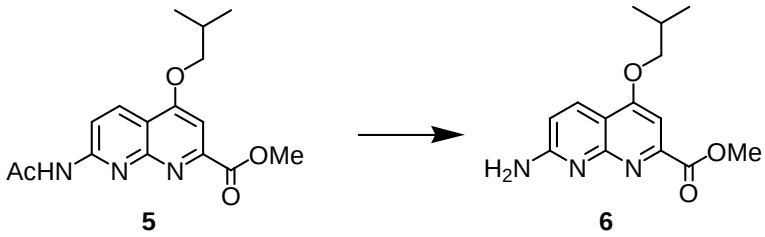
3 **4**

Fumarate derivative **2** (228 mmol, 67 g) was added to refluxing diphenylether (3 L at 260°C) (a dilution factor of 1g of the fumarate derivative to 50 mL of diphenylether was critical as a more concentrated solution gave impure products) and the mixture heated at the reflux temperature for 40 min. The reaction mixture was let to come back to RT then added to petroleum ether (8 L). The precipitated was triturated and filtered with two more litre of petroleum ether. The naphthyridone **4** was obtained as a black powder (87 %, 52 g) used without any further purification for the following Mitsunobu reaction. ^{1}H NMR (300 MHz, DMSO-d6) δ ppm = 11.73 (br s, 1H); 10.67 (s, 1H); 8.40 (d, ^{3}J= 8.7 Hz, 1H); 8.07 (d, ^{3}J= 8.7 Hz, 1H); 6.66 (s, 1H); 3.94 (s, 3H); 2.21 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d6) δ ppm = 177.1; 170.3; 162.2; 154.9;

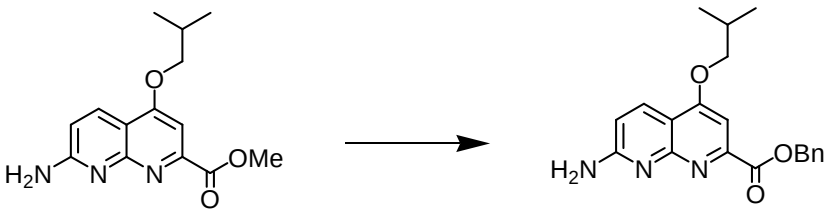
149.6; 138.6; 136.8; 117.1; 111.9; 111.4; 53.4; 24.4. HRMS (ES^+): *m/z* calcd for $C_{12}H_{12}N_3O_4$ $[M+H]^+$: 262.0828 found 262.0821.



In a dry 1 Litre round-bottom-flask placed under inert atmosphere, naphthyridone **4** (199 mmol, 52 g), freshly distilled 2-methyl propanol (219 mmol, 20.2 mL) and triphenylphosphine (219 mmol, 57.48 g) was suspended in 700 mL anhydrous THF (the naphthyridone was not soluble in THF before the addition of diisopropyl azodicarboxylate). Reaction mixture was cooled to 0°C (ice bath), then diisopropyl azodicarboxylate (219 mmol, 43.15 mL) was added to the mixture and let to stir at 0°C for 30 min and subsequently at RT for 24 h. Solvents are removed by rotary evaporation, and residue was recrystallised from methanol. Product was dried under reduced pressure to yield 29.7 g (47%, white powder) of naphthyridine derivative **5**. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm = 8.90 (br s, 1H); 8.58 (d, ^{3}J = 8.8 Hz, 1H); 8.53 (d, ^{3}J = 8.8 Hz, 1H); 7.55 (s, 1H); 4.06 (d, ^{3}J = 6.2 Hz, 2H); 4.04 (s, 3H), 2.28-2.24 (1H, m); 1.12 (d, ^{3}J = 6.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm = 170.3; 165.9; 163.4; 155.1; 151.5; 133.9; 115.9; 114.5; 101.0; 75.5; 53.0; 28.1; 24.9; 19.1. HRMS (ES^+): *m/z* calcd for $C_{16}H_{20}N_3O_4$ $[M+H]^+$: 318.1454 found 318.1444.

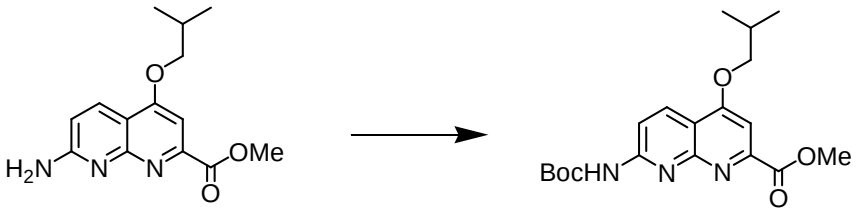


In a 250 mL round bottomed flask equipped with a large magnetic stirrer, naphthyridine derivative **5** (9.5 mmol, 3 g) was dissolved in methanol (100 mL). Reaction mixture was cooled to 0°C (ice bath), then H_2SO_4 (47.3 mmol, 2.5 mL) was added dropwise. After one hour at 0°C, the reaction mixture was allowed to warm and let at RT overnight. The mixture was then neutralised with a saturated $NaHCO_3$ solution and extracted with dichloromethane. Organic layers were washed with distilled water, brine and dried over $MgSO_4$. Solvents were removed to yield 2.1 g (80%, white powder) of amino naphthyridine derivative **6**. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm = 8.27 (d, ^{3}J = 8.8 Hz, 1H); 7.41 (s, 1H); 6.82 (d, ^{3}J = 8.8 Hz, 1H); 5.31 (s, 2H); 4.06 (d, ^{3}J = 6.2 Hz, 2H); 4.04 (s, 3H); 2.28-2.20 (m, 1H); 1.10 (d, ^{3}J = 6.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm = 166.4; 163.1; 160.3; 157.1; 150.7; 132.4; 112.8; 111.0; 99.7; 75.1; 52.7; 28.1; 19.1. HRMS (ES^+): *m/z* calcd for $C_{14}H_{18}N_3O_3$ $[M+H]^+$: 276.1348 found 276.1341.



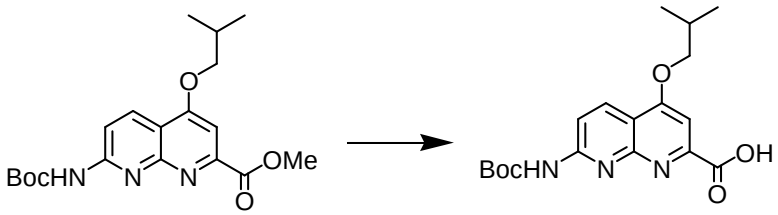
6 **7**

In a 100 mL round bottomed flask, amino naphthyridine derivative **6** (10.9 mmol, 3 g) was dissolved in dry benzyl alcohol (0.27 mol, 28 mL). Then triethylamine (54.5 mmol, 7.6 mL) was added, and the mixture was heated at 60°C for 24 hours. The solvents were removed under high vacuum and the residue was purified by chromatography. The benzyl ester **7** was obtained as a white solid (95 %, 3.49 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm = 8.23 (d, ^{3}J = 8.8 Hz, 1H); 7.54-7.51 (m, 2H); 7.43 (s, 1H); 7.40-7.32 (m, 3H); 6.93 (d, ^{3}J = 8.8 Hz, 1H); 6.11 (br s, 2H); 5.52 (s, 2H); 3.98 (d, ^{3}J = 6.6 Hz, 2H); 2.23 (m, 1H); 1.09 (d, ^{3}J = 6.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm = 165.7; 163.6; 156.3; 152.6; 152.1; 151.1; 134.1; 114.7; 113.9; 100.0; 82.3; 76.4; 28.2; 28.1; 19.1. HRMS (ES^+): *m/z* calcd for $C_{20}H_{22}N_3O_3$ $[M+H]^+$: 352.1661 found 351.1583.



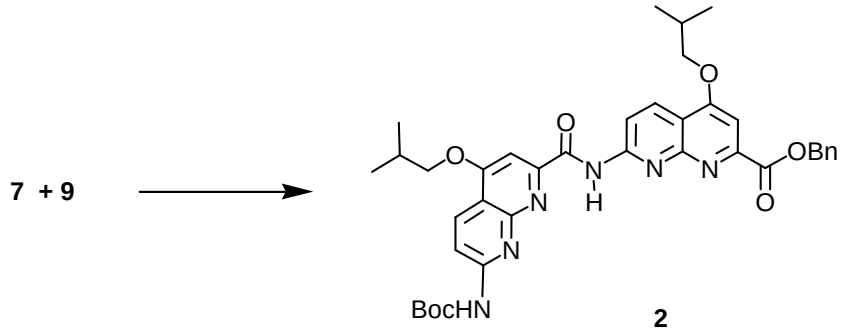
6 **8**

Amino naphthyridine derivative **6** (10.9 mmol, 3 g) and di-*tert*-butyl dicarbonate (21.8 mmol, 4.7 g) were dissolved in 100 mL of dioxane. The mixture was heated to reflux for 4 hours (protection was followed by TLC). Dioxane was removed under reduced pressure and the residue was purified by silica chromatography. The boc-protected naphthyridine **8** was obtained as a white powder (80 %, 3.27 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm = 8.52 (d, ^{3}J = 8.8 Hz, 1H); 8.32 (d, ^{3}J = 8.8 Hz, 1H); 7.57 (br s, 1H); 7.52 (s, 1H); 4.04 (d, ^{3}J = 6.6 Hz, 1H); 4.03 (s, 3H); 2.27 (m, 1H); 1.56 (s, 9H); 1.12 (d, ^{3}J = 6.8 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm = 165.9; 163.3; 155.3; 154.8; 152.0; 151.4; 133.5; 113.8; 100.6; 81.7; 75.4; 66.9; 52.9; 28.1; 28.0; 19.0. HRMS (ES^+): *m/z* calcd for $C_{19}H_{26}N_3O_5$ $[M+H]^+$: 376.1872 found 376.1862.



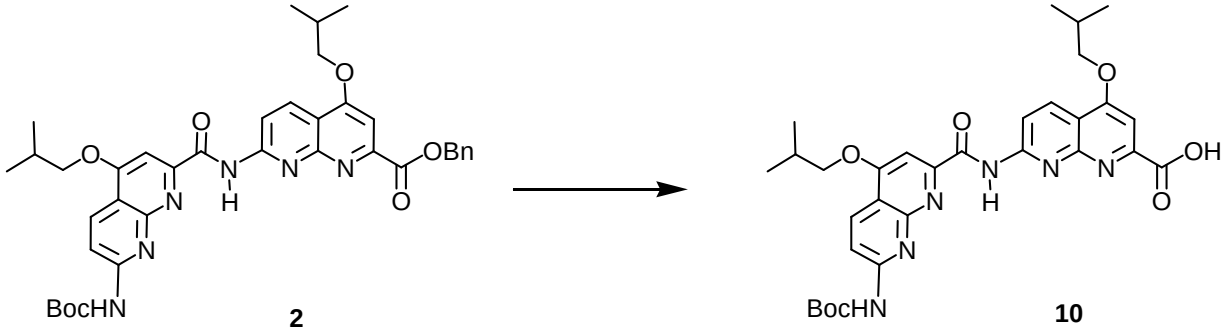
8 **9**

Naphthyridine derivative **8** (8.0 mmol, 3 g) in a 100 mL solution of dioxane/water (8/2) was introduced in a 250 mL round bottomed flask equipped with a large magnetic stirrer. Sodium hydroxide (24 mmol, 0.96 g) was added to this mixture. The resulting slurry was stirred at RT for 3h. Reaction was then quenched by addition of 10 mL acetic acid, and solvents were removed under reduced pressure. The residue was dissolved in 150 mL of dichloromethane. Organic layer was washed with distilled water, brine and dried over $MgSO_4$. Solvents were removed to yield 2.88 g (quantitative, white powder) of acid naphthyridine derivative **9**. ^{1}H NMR (300 MHz, DMSO-d6) δ ppm = 10.38 (s, 1H), 8.54 (d, ^{3}J = 9 Hz, 1H); 8.18 (d, ^{3}J = 9 Hz, 1H); 7.48 (s, 1H); 4.10 (d, ^{3}J = 6.2 Hz, 2H); 2.19 (m, 1H); 1.51 (s, 9H); 1.07 (d, ^{3}J = 6.4 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm = 175.6; 165.5; 163.8; 156.4; 152.5; 152.2; 151.2; 134.1; 114.7; 113.7; 100.1; 82.2; 76.4; 28.1; 19.1. HRMS (ES$^+$): *m/z* calcd for $C_{18}H_{24}N_3O_5$ $[M+H]^+$: 362.1716 found 362.1717.



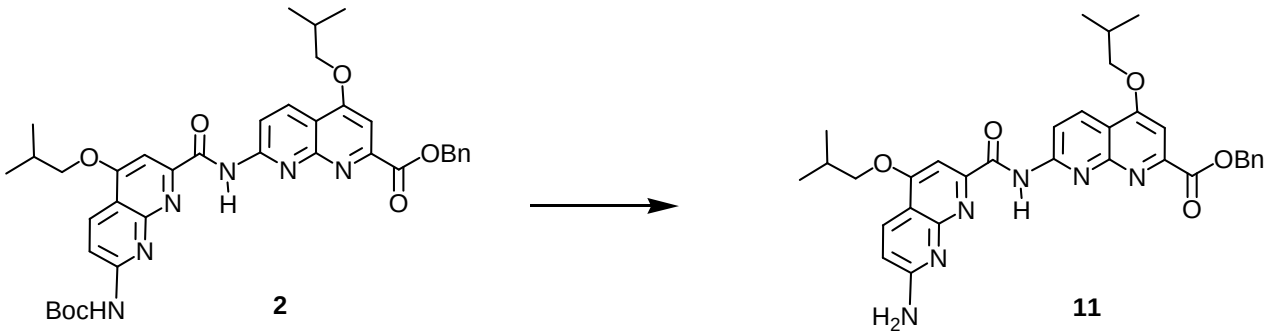
2

In a 100 mL round bottomed flask, naphthyridine acid derivative **9** (1.76 mmol, 0.634 g), amino naphthyridine derivative **7** (1.76 mmol, 0.616 g) and PyBOP (3.52 mmol, 1.830 g) were dissolved in 40 mL of dry dichloromethane. Then, triethylamine (7.04 mmol, 0.98 mL) was added and the reaction mixture was let at RT for 12 hours. The solvents were removed under reduced pressure and the residue was purified by silica chromatography. The naphthyridine dimer **2** was obtained as a white solid (80 %, 0.98 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm = 11.29 (br s, 1H); 8.77 (d, ^{3}J = 8.9 Hz, 1H); 8.67 (d, ^{3}J = 8.9 Hz, 1H); 8.55 (d, ^{3}J = 9.1 Hz, 1H); 8.35 (d, ^{3}J = 9.1 Hz, 1H); 7.72-7.33 (m, 7H); 5.51 (s, 2H); 4.10 (d, ^{3}J = 6.8 Hz, 2H); 4.05 (d, ^{3}J = 6.4 Hz, 2H); 2.30 (m, 2H); 1.60 (s, 9H); 1.14 (d, ^{3}J = 6.8 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm = 166.5, 164.8, 164.3, 164.1, 156.5, 156.1, 155.6, 154.9, 153.6, 153.0, 153.0, 136.6, 134.9, 134.7, 129.6, 129.4, 129.2, 116.1, 115.7, 115.121, 114.7, 102.0, 99.3, 82.8, 76.5, 76.4, 68.6, 29.2, 20.1. HRMS (ES$^+$): *m/z* calcd for $C_{38}H_{42}N_6O_7Na$ $[M+Na]^+$: 717.3013 found 717.3009.

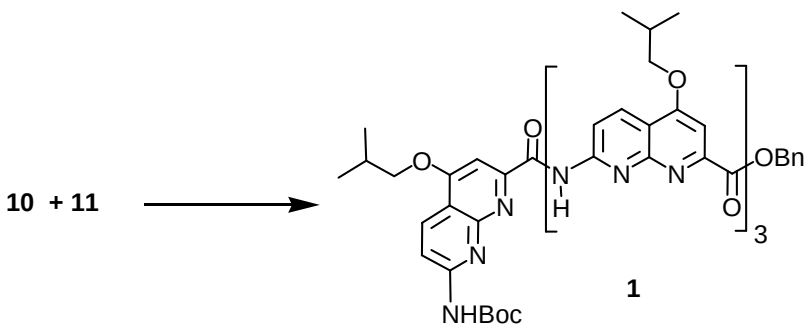


2 **10**

Pd/ 10 % on carbon (15 % w/w, 75 mg) previously activated by heating under *vacuum* with a heat gun was added to a solution of naphthyridine dimer **2** (0.72 mmol, 0.5 g) in dry DMF (50 mL). The flask was evacuated then filled with hydrogen (1 atm) and the reaction mixture was stirred for 6h at RT. The Pd catalyst was removed by filtration, washed with dichloromethane and the filtrate was evaporated under reduced pressure to give the pure acid derivative **10** (90 %, 0.391 g) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm = 8.84 (d, ^{3}J = 9.2 Hz, 1H); 8.80 (d, ^{3}J = 9.4 Hz, 1H); 8.78 (d, ^{3}J = 9.2 Hz, 1H); 8.57 (d, ^{3}J = 9.4 Hz, 1H); 7.93 (s, 1H); 7.78 (s, 1H); 4.23 (d, ^{3}J = 6.8 Hz, 2H); 4.20 (d, ^{3}J = 6.8 Hz, 2H); 2.34 (m, 2H); 1.63 (s, 9H); 1.15 (d, ^{3}J = 6.6 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm = 164.9; 164.1; 163.5; 155.2; 154.6; 153.9; 152.4; 152.0; 150.4; 134.6; 133.9; 115.7; 115.3; 114.3; 114.0; 99.5; 98.5; 82.1; 77.2; 76.1; 75.7; 28.2; 28.1; 19.1; 19.1. HRMS (ES^+): *m/z* calcd for $C_{31}H_{37}N_6O_7$ $[M+H]^+$: 605.2724 found 605.2738.



Trifluoroacetic acid (3 mL) was added dropwise to a solution of naphthyridine dimer **2** (0.72 mmol, 0.5 g) in 15 mL of dichloromethane under nitrogen at 0°C (ice bath). Then, the resultant mixture was stirred at RT for 5 h. The volatiles were removed under reduced pressure to give a solid which was redissolved in dichloromethane and washed two times with a saturated solution of $NaHCO_3$, water then brine. The organic layers were dry over $MgSO_4$ then the volatiles were removed under reduce pressure to give the amine derivative **11** as white solid (85 %, 0.363 g). ^{1}H NMR (300 MHz, $CDCl_3$) δ ppm =11.34 (s, 1H); 8.79 (d, ^{3}J = 9Hz, 1H); 8.68 (d, ^{3}J = 9Hz, 1H); 8.35 (d, ^{3}J = 8.9 Hz, 1H); 7.64 (s, 1H); 7.62 (s, 1H); 7.57 (s, 2H); 7.41 (m, 3H); 6.84 (d, 1H); 5.53 (s, 2H); 5.17 (br s, 2H); 4.08 (q, 4H); 2.3 (m, 2H); 1.16 (d, ^{3}J=3.4Hz, 6H); 1.14 (d, ^{3}J=3.4z, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ ppm = 166.2; 164.6; 164.4; 164.1; 161.8; 156.7; 156.4; 155.0; 152.6; 152.0; 136.5; 134.7; 129.6; 129.5; 129.3; 129.2; 116.0; 115.5; 114.7; 111.8; 101.9; 98.1; 78.1; 76.3; 76.1; 68.6; 29.0; 20.1; 20.0. HRMS (ES^+): *m/z* calcd for $C_{33}H_{35}N_6O_5$ $[M+H]^+$: 595.2669 found 595.2654.



In a 50 mL round bottomed flask, dimer acid **10** (0.5 mmol, 0.3 g), dimer amine **11** (0.5 mmol, 0.295 g) and PyBOP (1 mmol, 0.52 g) were dissolved in 20 mL of dry dichloromethane. Then, triethylamine (2.5 mmol, 350 µL) was added and the reaction mixture was let at RT for 12 h. The solvents were removed under reduced pressure and the residue was purified by silica chromatography. The naphthyridine tetramer **1** was obtained as a white solid (70 %, 0.413 g). ^{1}H NMR (300 MHz, Pyr-d5) δ ppm = 12.0 (br s, 1H); 11.58 (br s, 1H); 11.43 (br s, 1H); 8.88 (d, ^{3}J = 8.8 Hz, 1H); 8.76 (d, ^{3}J = 8.8 Hz, 1H); 8.73 (d, 1H); 8.64 (d, ^{3}J = 8.8 Hz, 1H); 8.57 (d, ^{3}J = 8.8 Hz, 1H); 8.47 (d, ^{3}J = 8.8 Hz, 1H); 8.44 (d, ^{3}J = 9.4 Hz, 1H); 8.39 (d, ^{3}J = 9.4 Hz, 1H); 8.08 (s, 1H); 8.07 (s, 1H); 7.88 (s, 1H); 7.64 (s, 1H); 7.44-7.37 (m, 2H); 7.29-7.16 (m, 3H); 5.08 (s, 2H); 4.20 (d, 2H); 4.17 (d, 2H); 4.04 (d, 4H); 2.30 (m, 4H); 1.30 (s, 9H); 1.25-1.12 (4xd, 4x6H). HRMS MS (ES^{+}): *m/z* calcd for $C_{192}H_{204}N_{36}O_{33}Na_2$ $[3M+2Na]^{2+}$: 1793.76 found 1794.46.

References

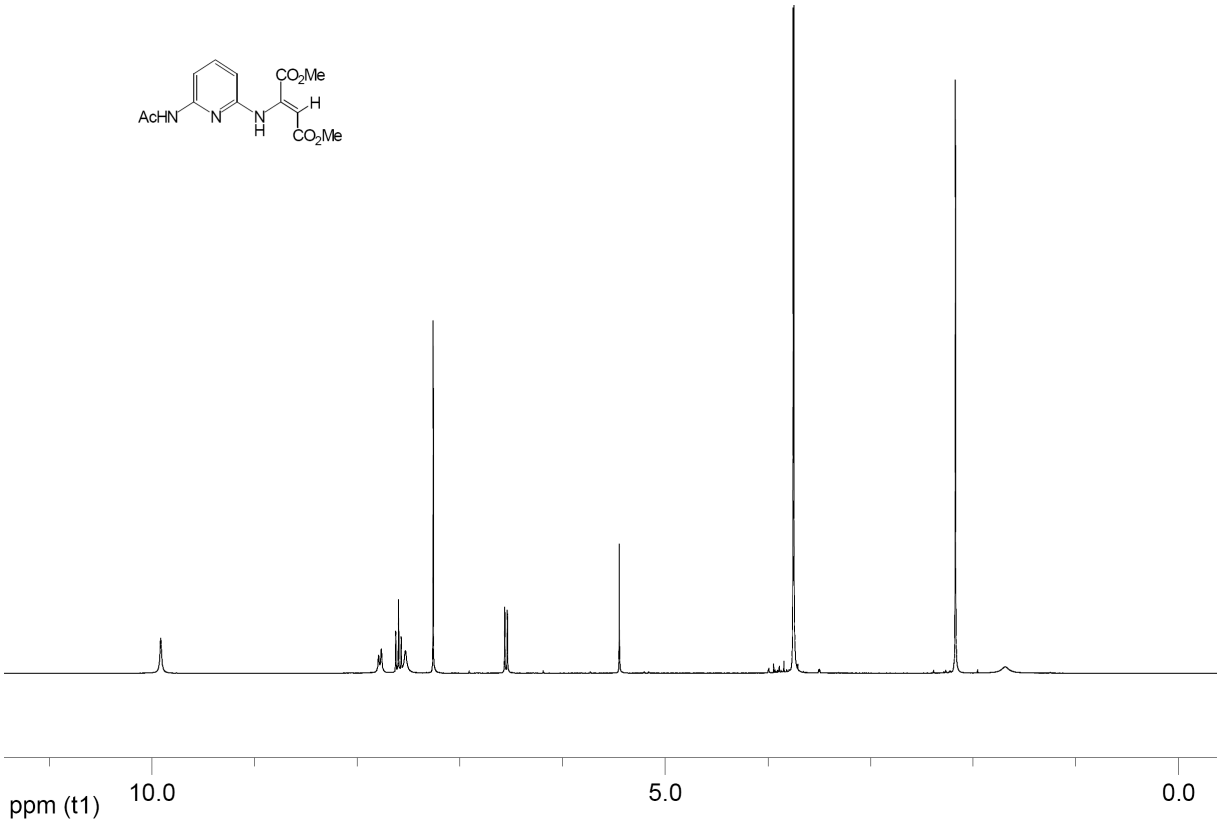
[1] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112 - 122.

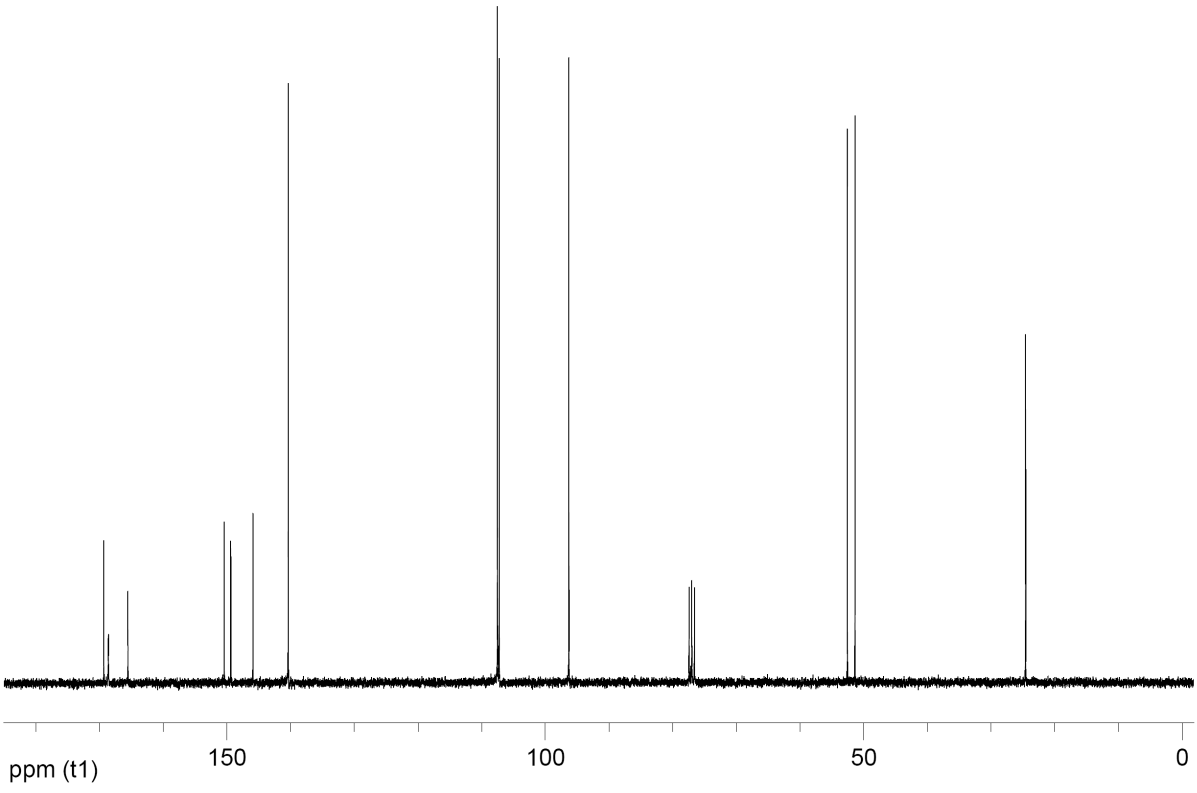
[2] P. v. d. Sluis & A. L. Spek, *Acta Cryst.* **1990**, *A46*, 194 - 201.

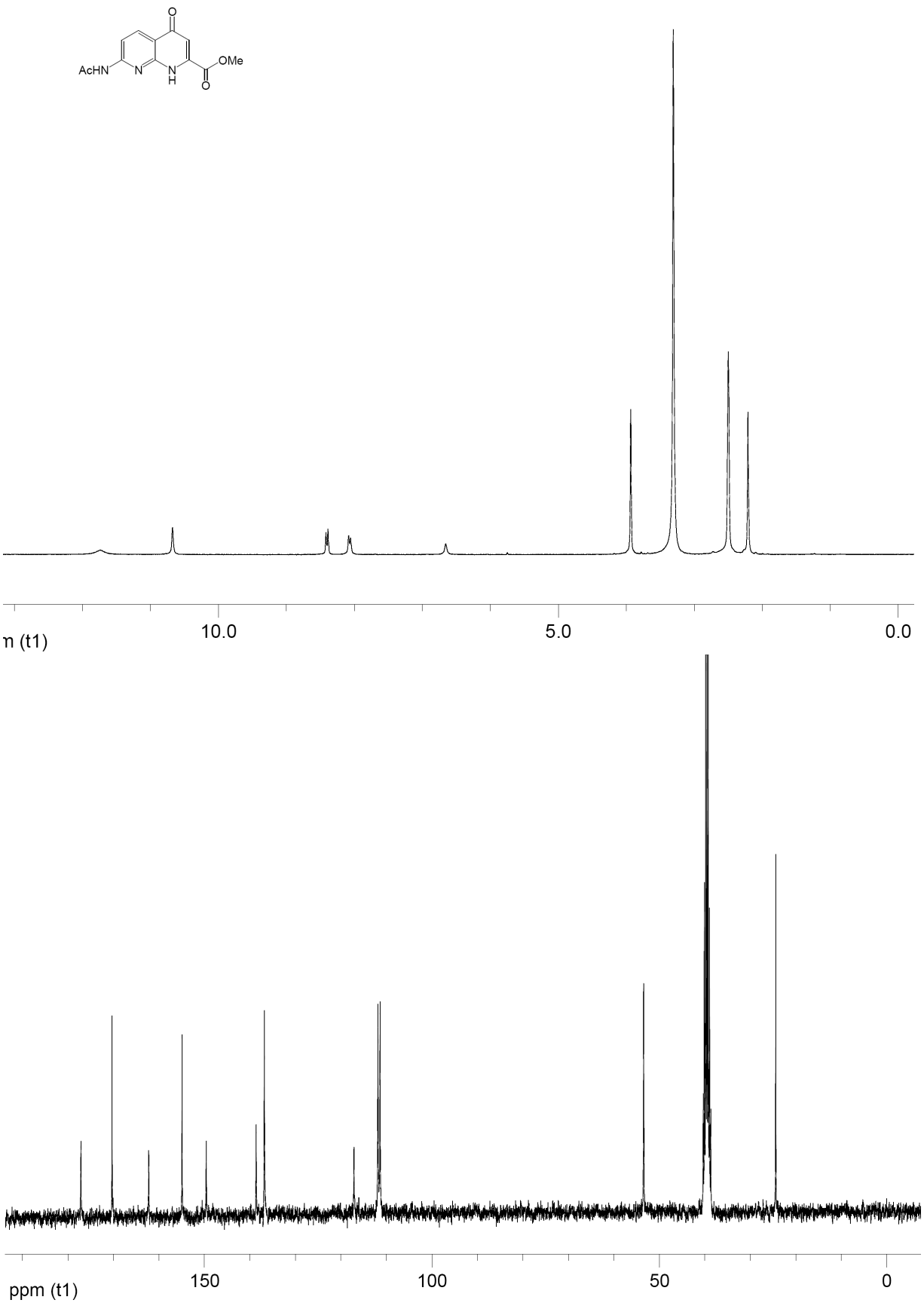
[3] Welter, R. *Acta Cryst.* **2006,** *A62*, s252. The CRYSTALBUILDER project: an easy way for single crystal structure analysis.

[4] D. Wan, K. Satoh, M. Kamigaito *Macromolecules* **2006,** *39*, 6882 - 6886.

NMR spectra of all relevant synthetic intermediates and title compounds.



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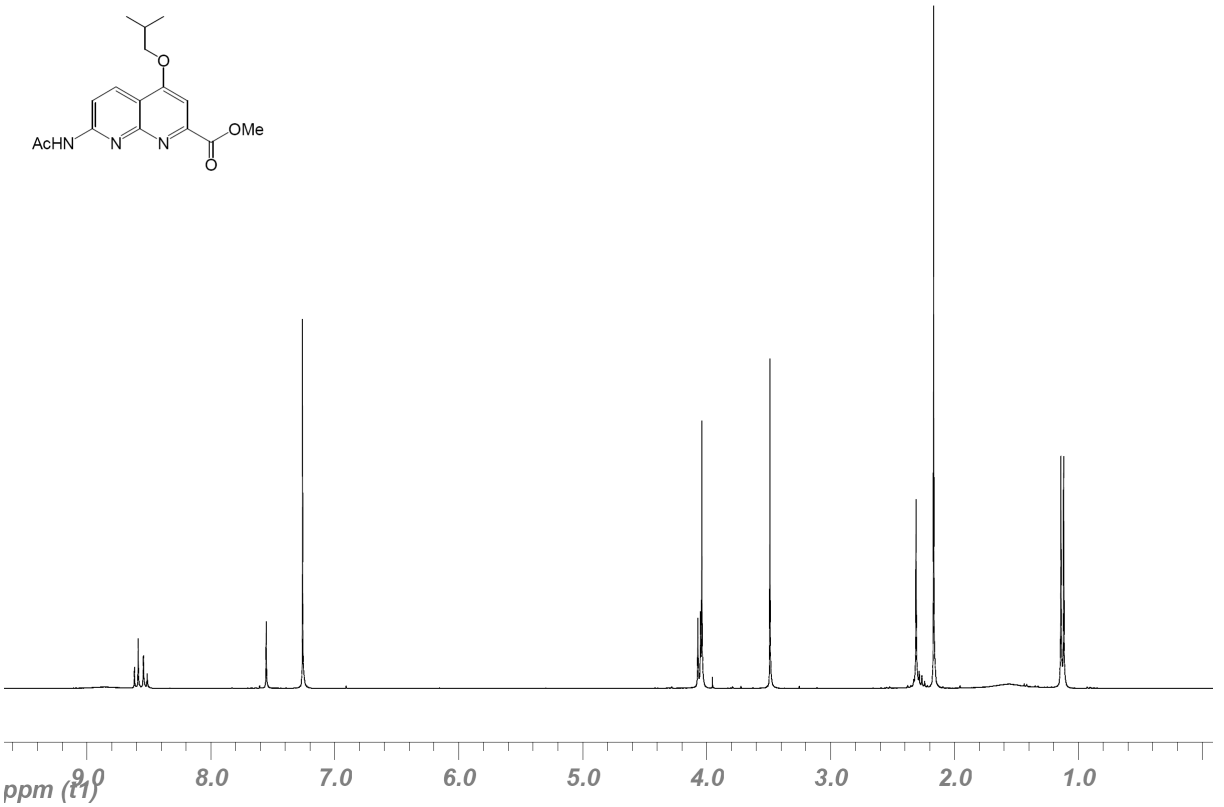
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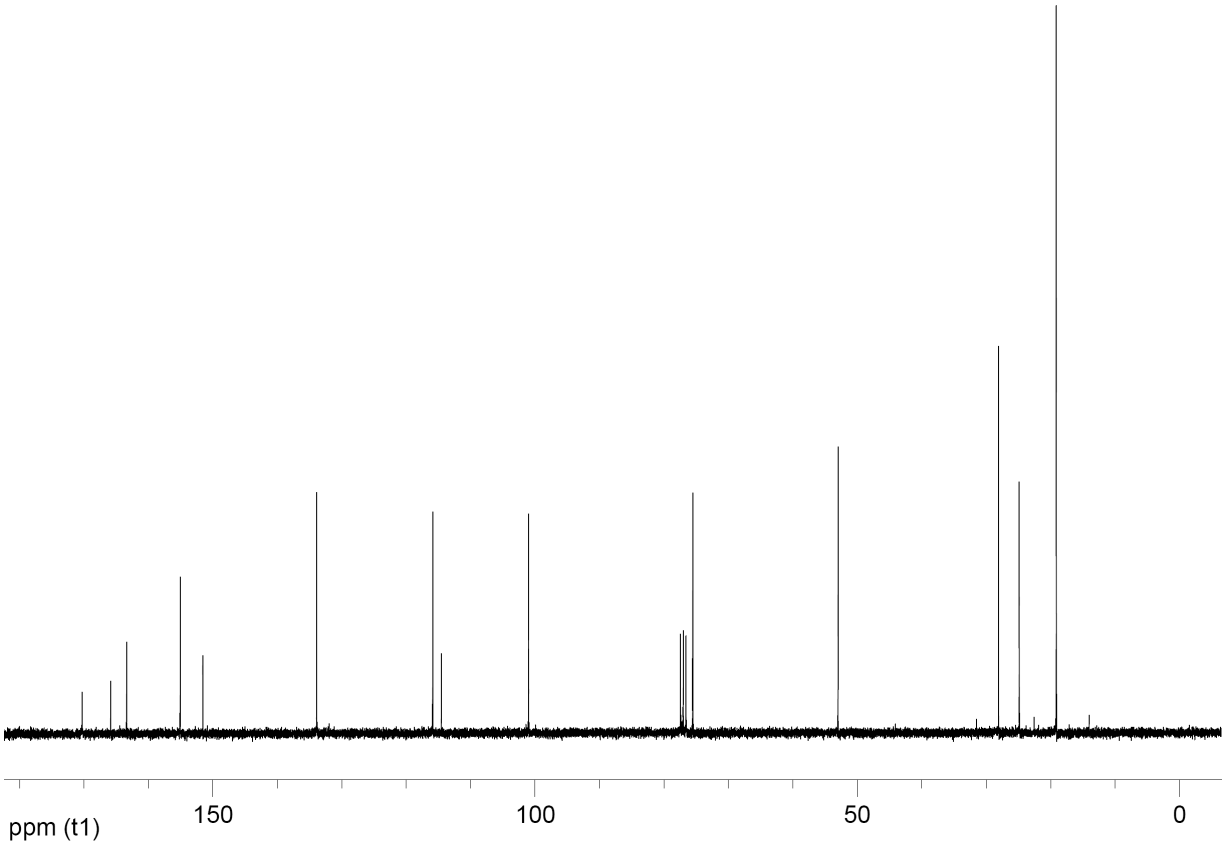
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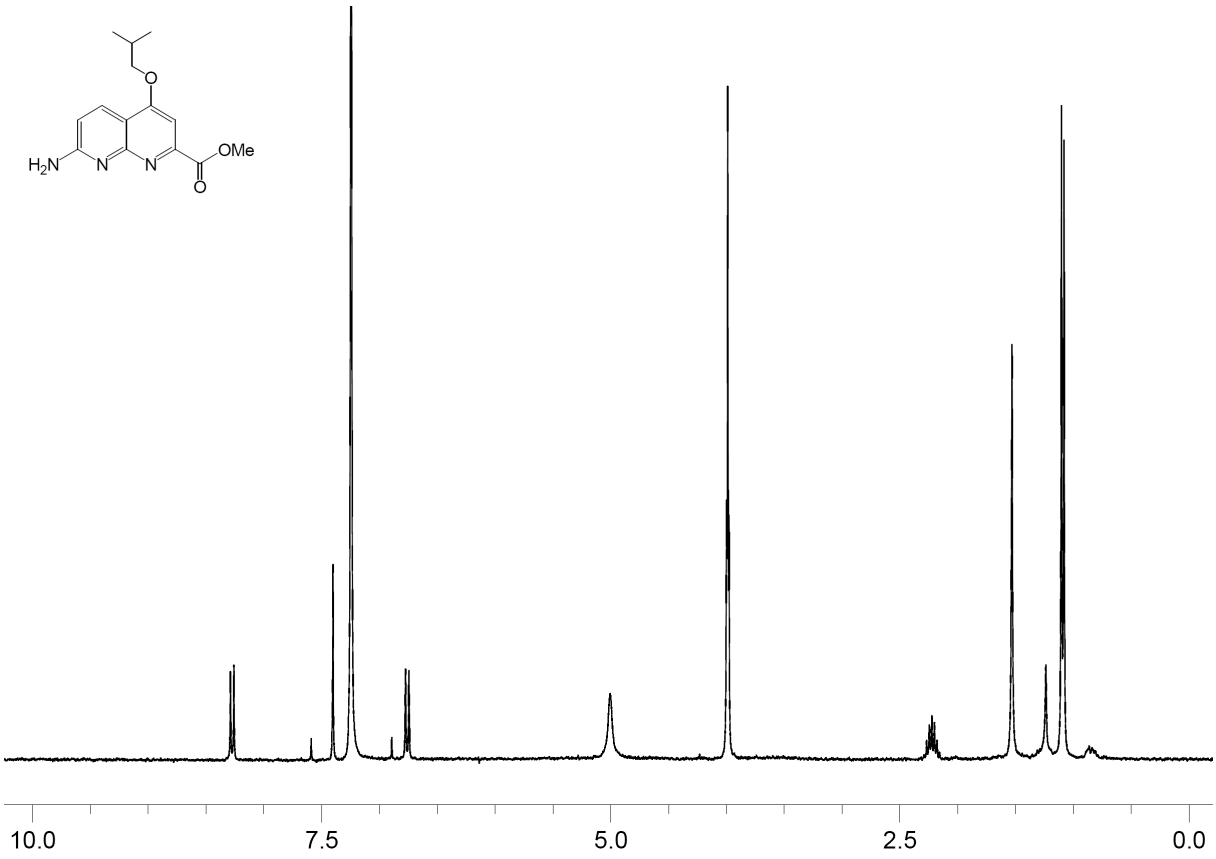
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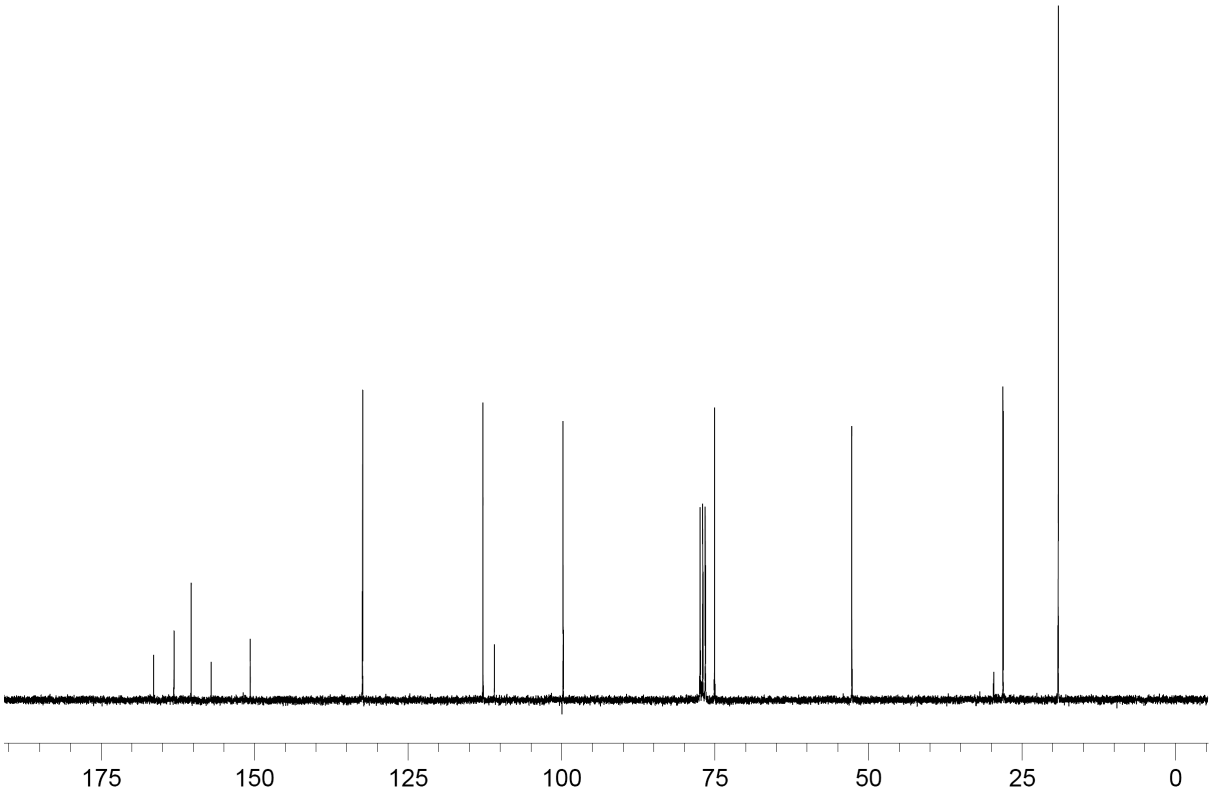
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75
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25
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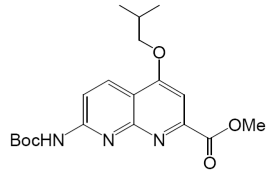
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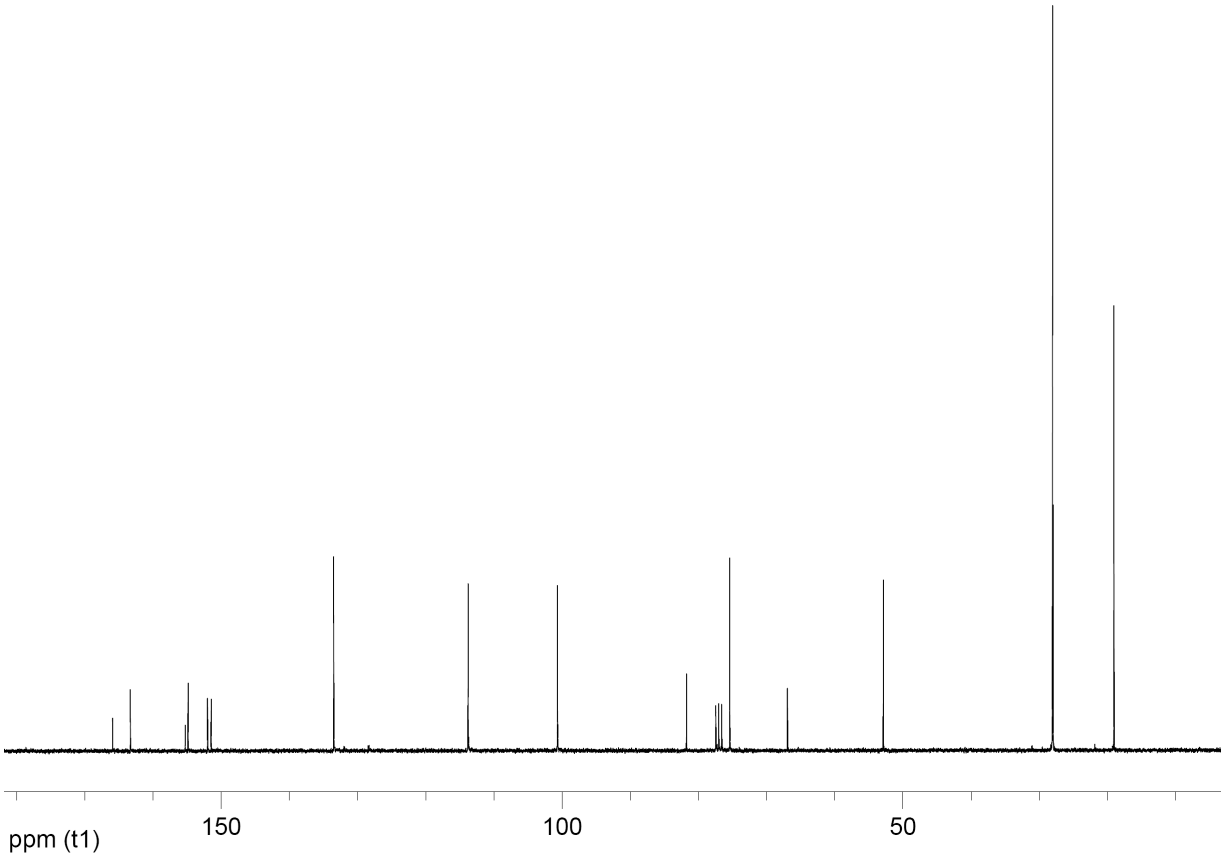
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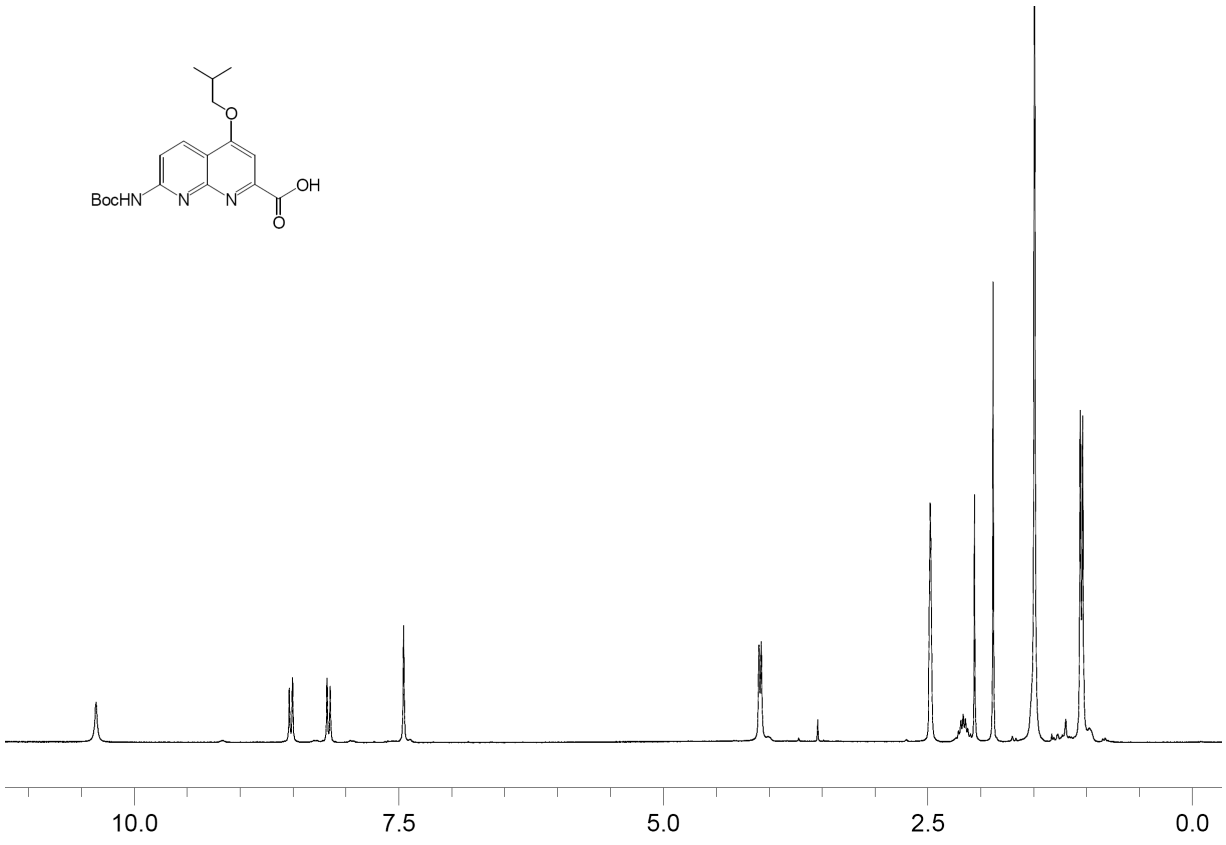
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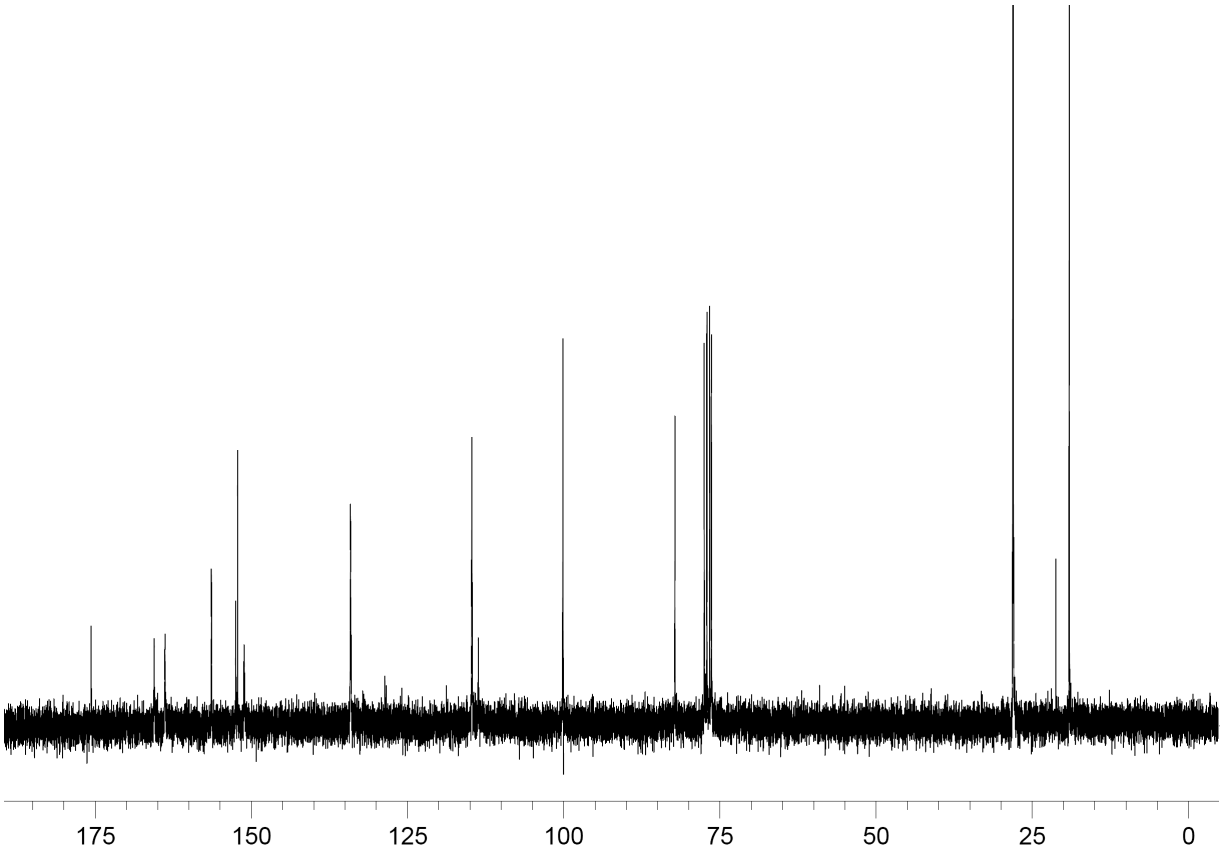
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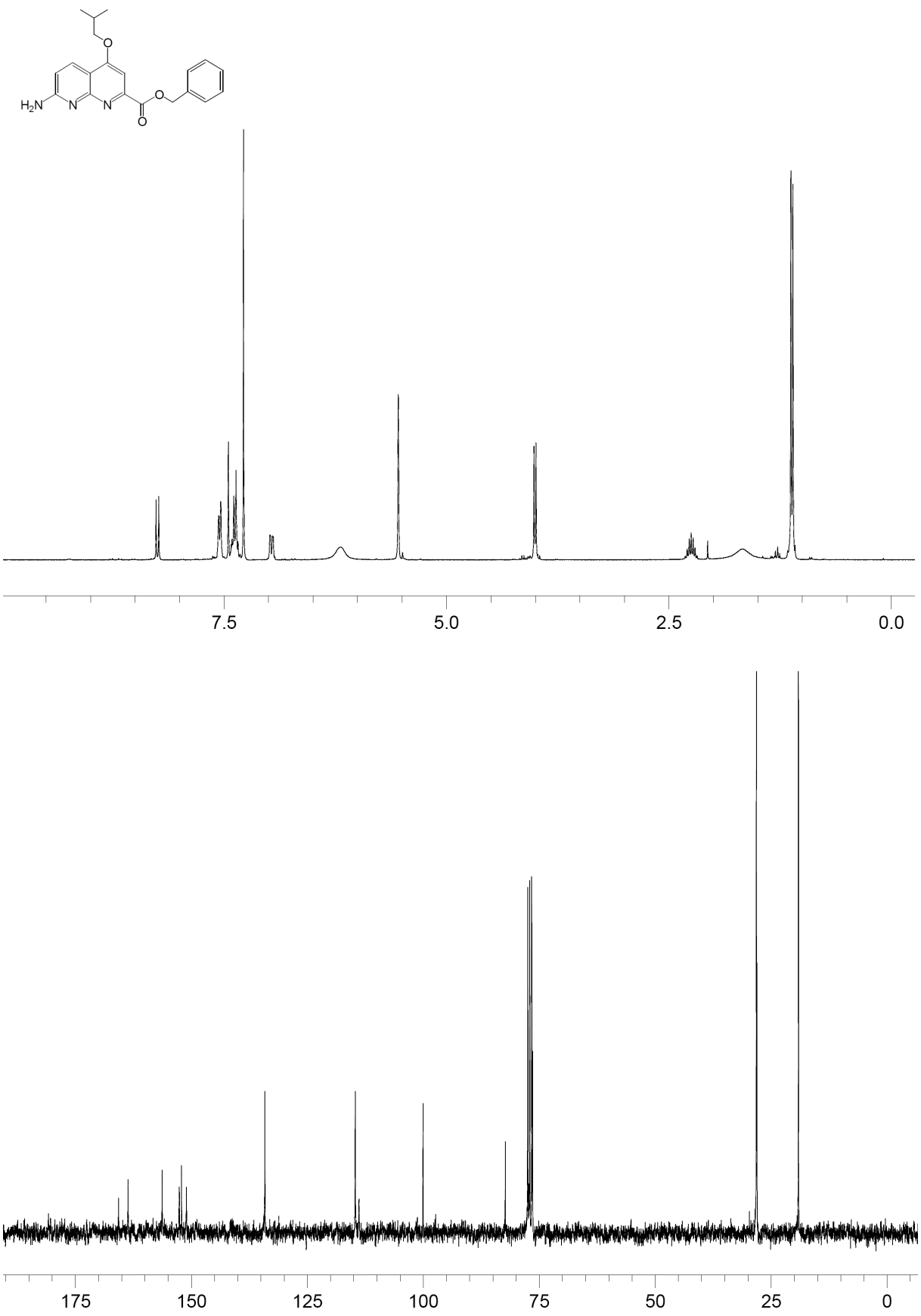
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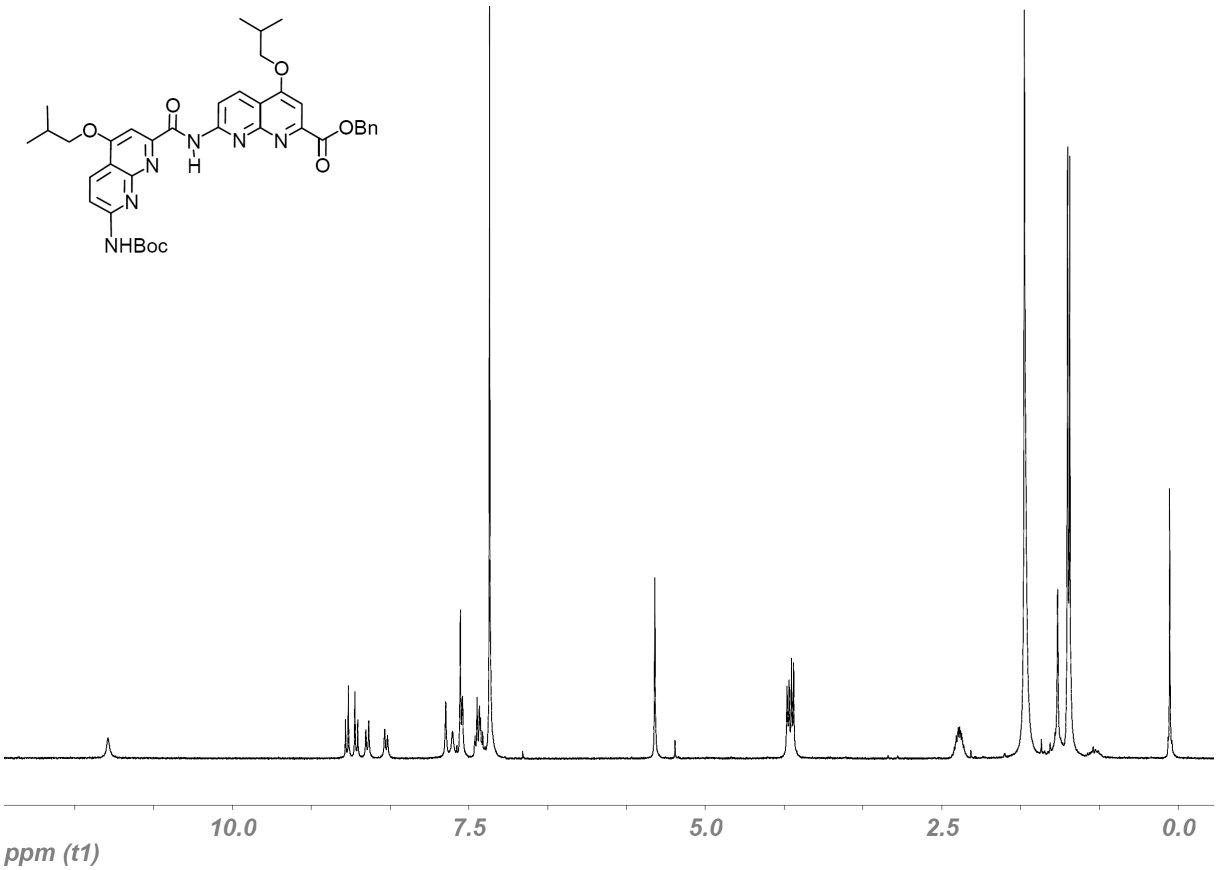
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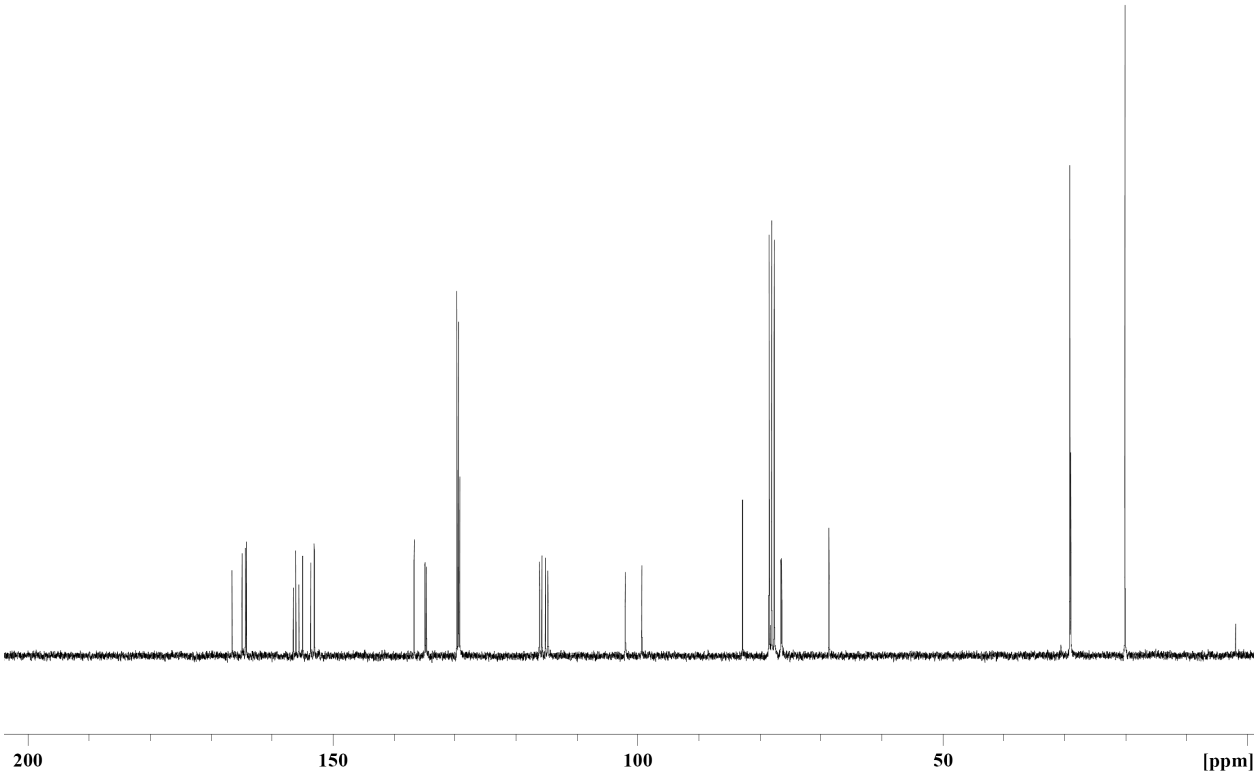
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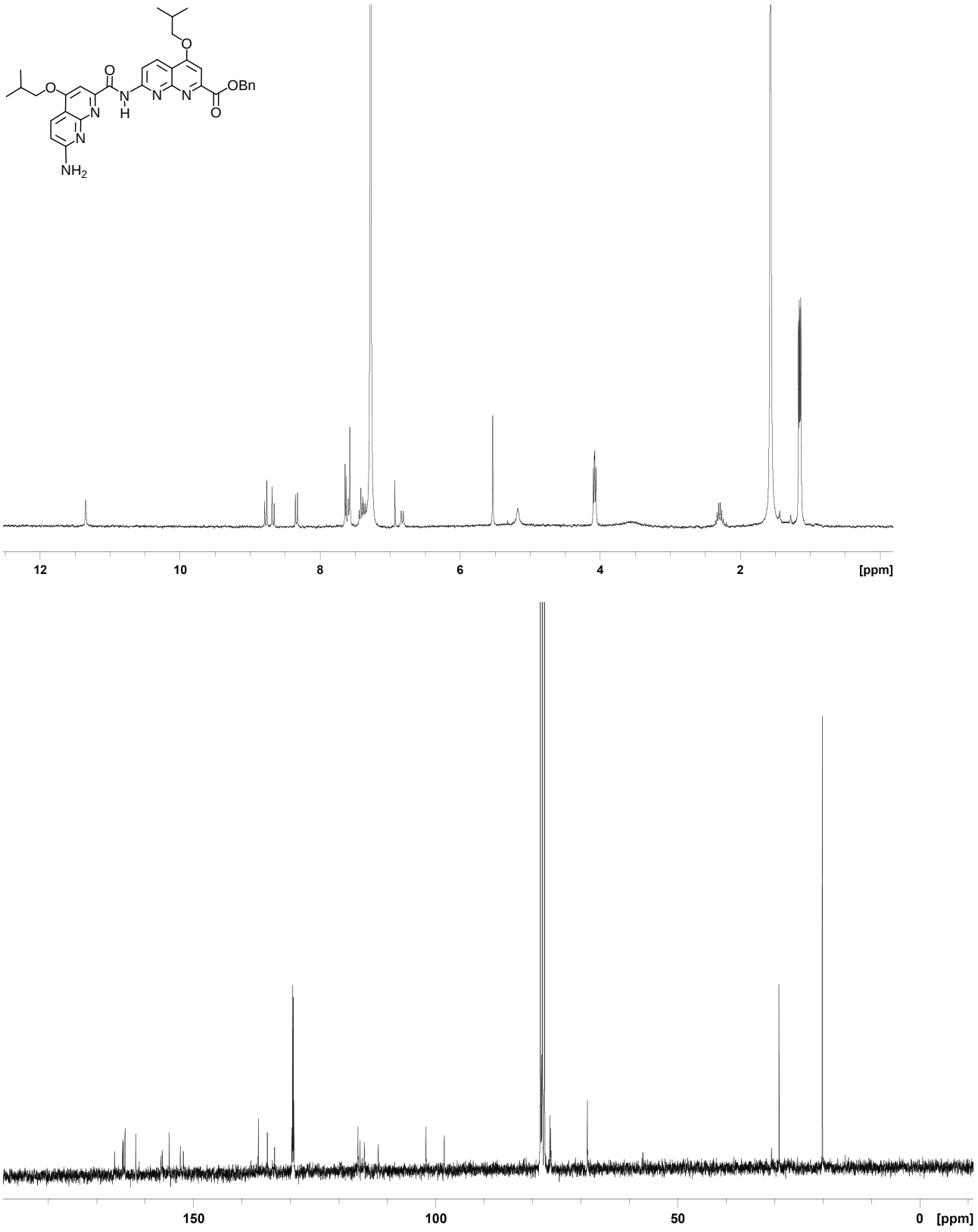
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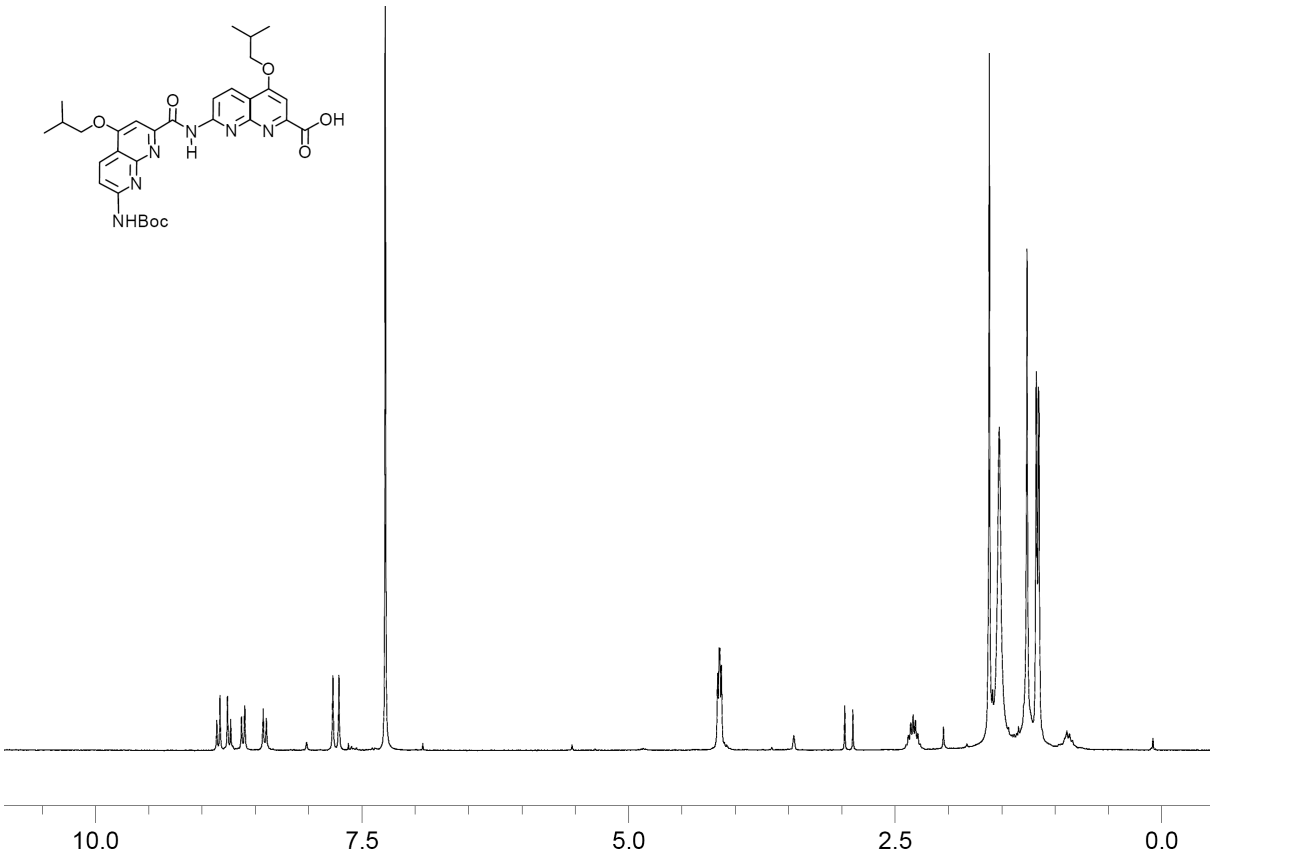
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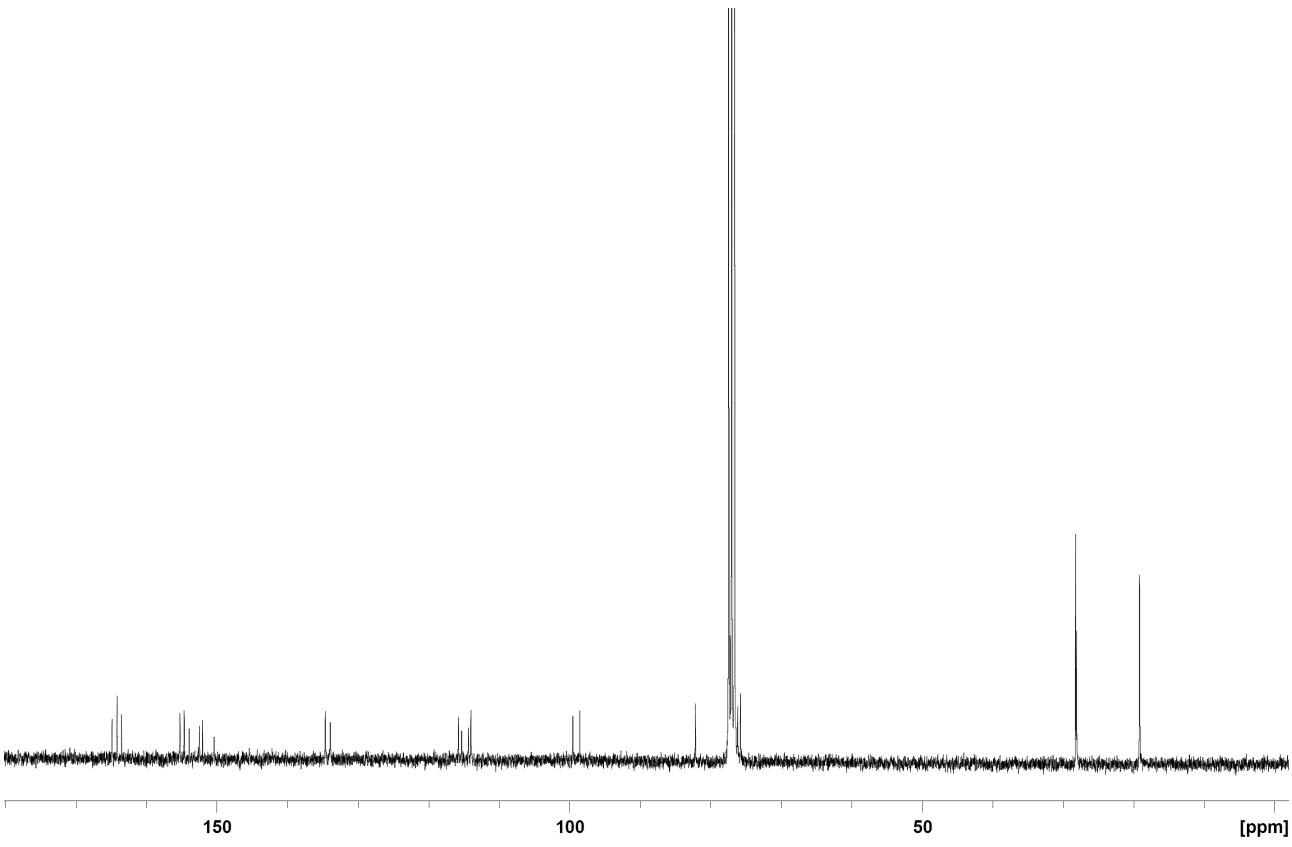
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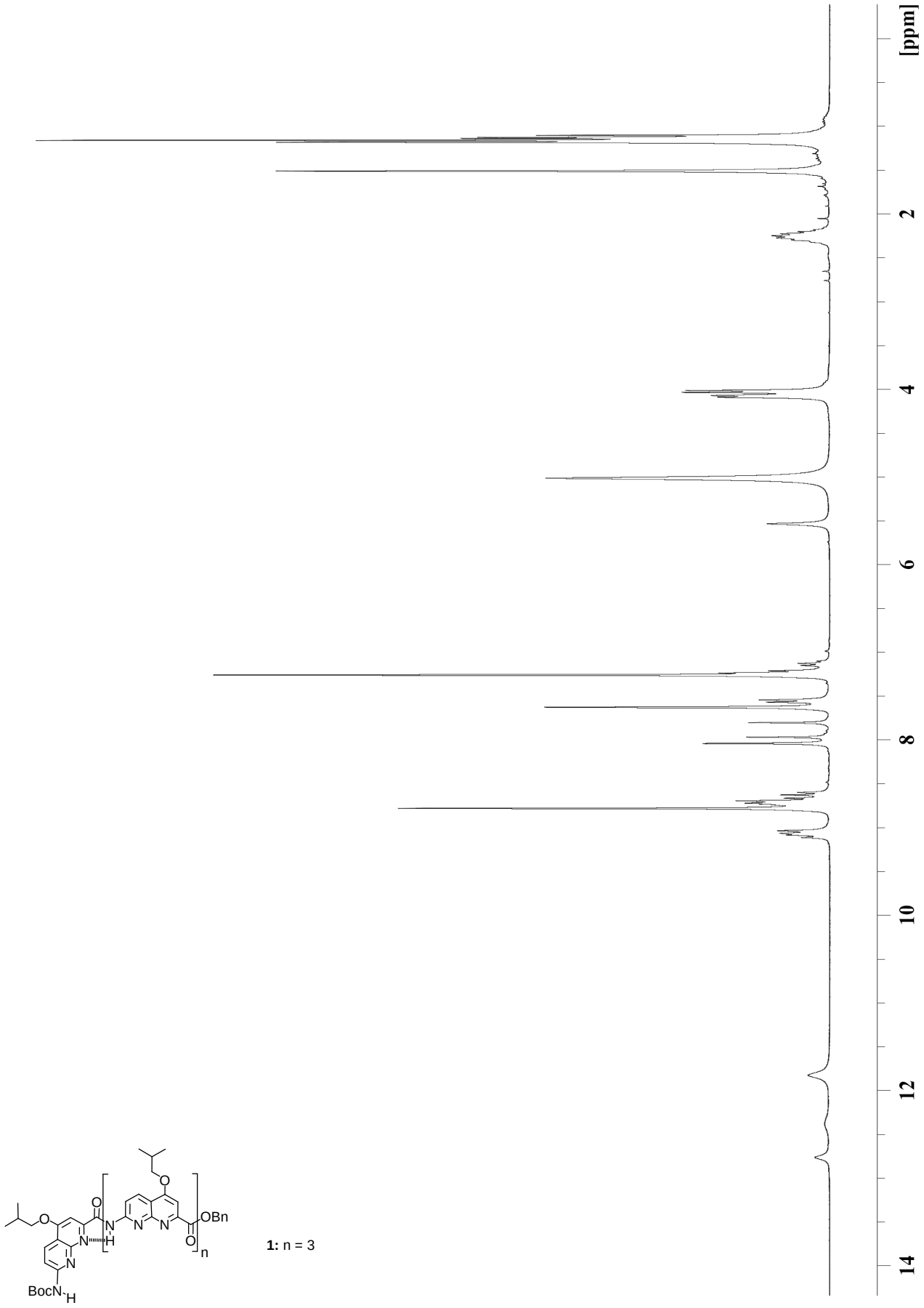
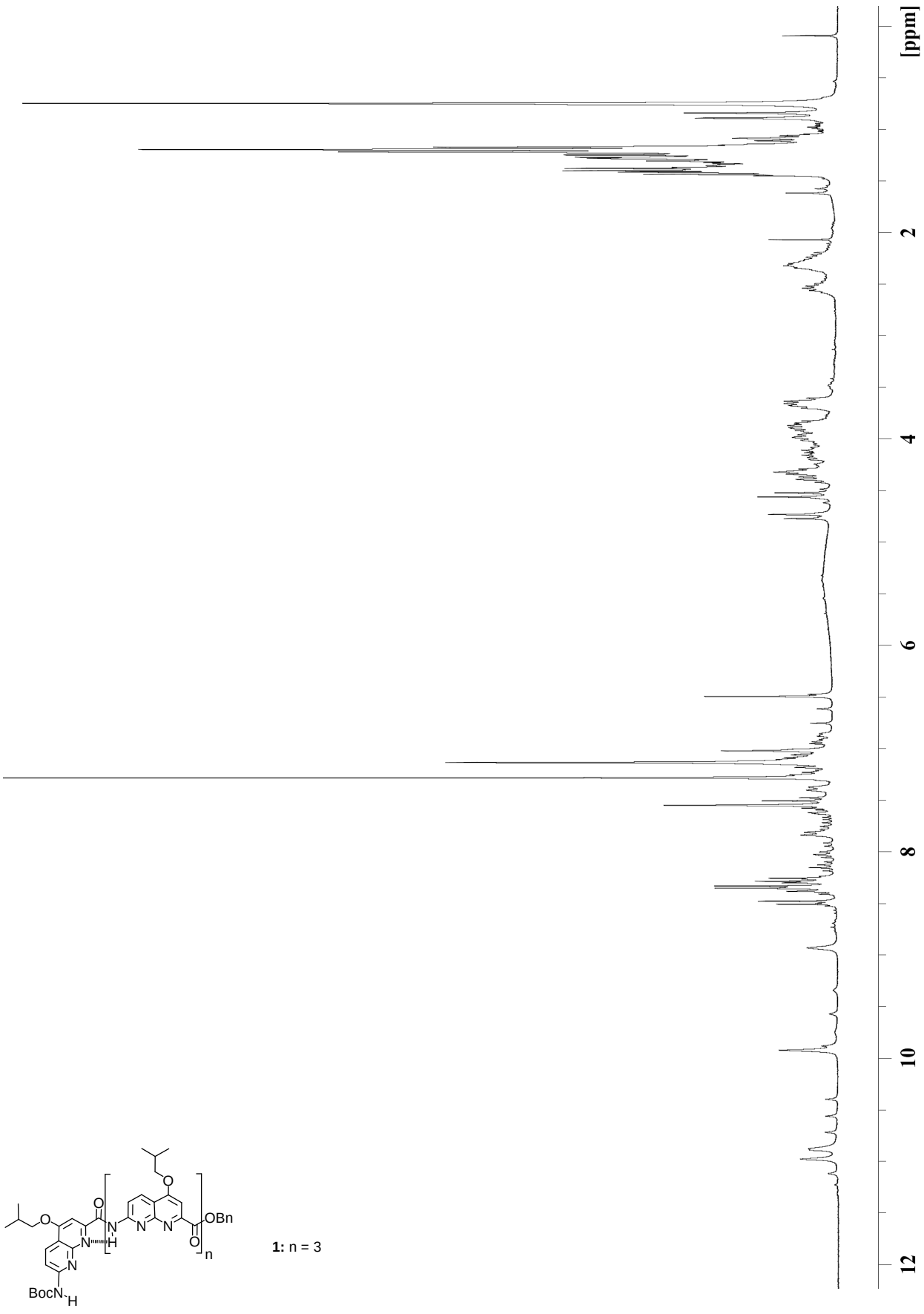
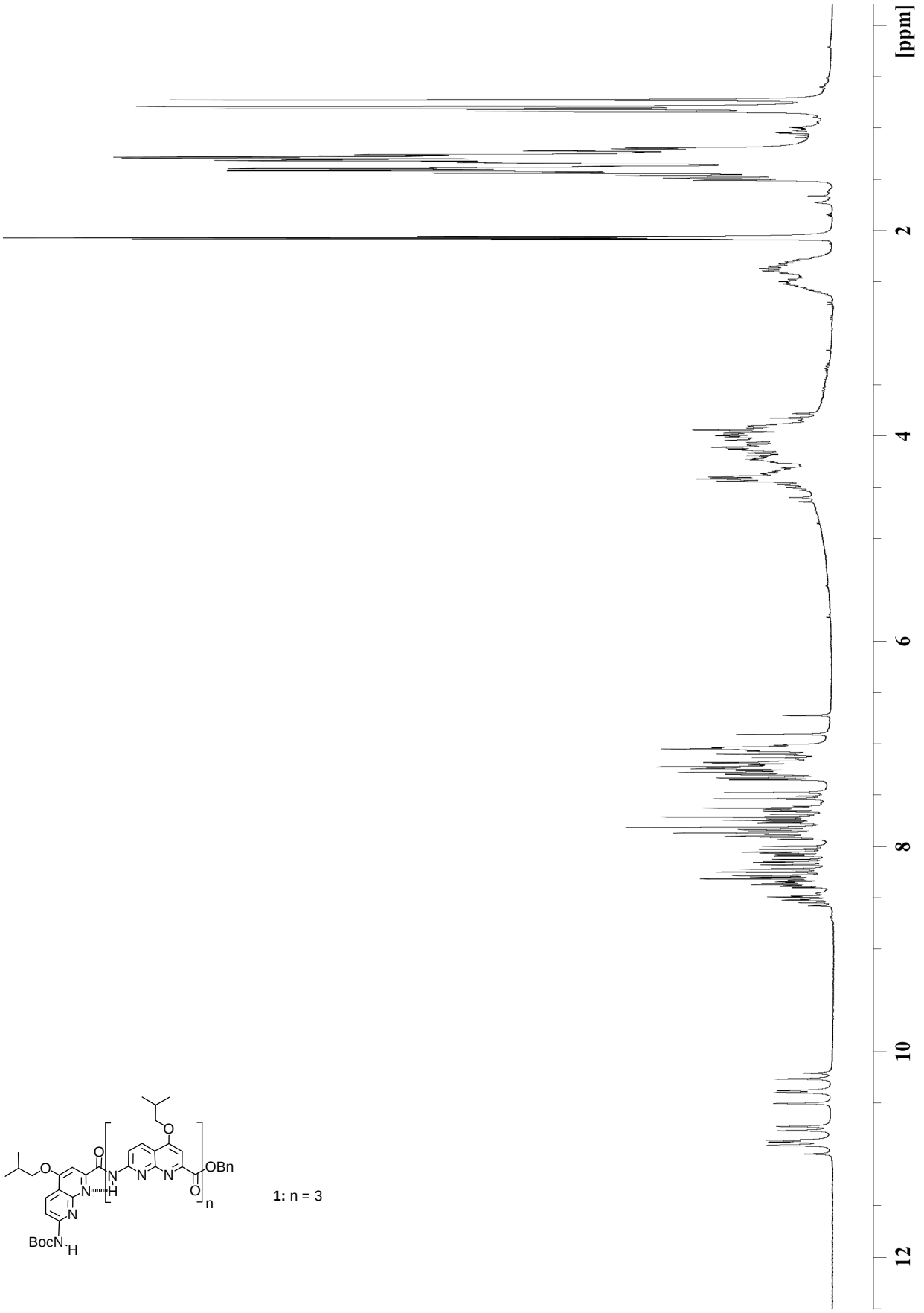


^{1}H NMR spectrum of tetramer **1** in d5-pyridine.



^{1}H NMR spectrum of tetramer **1** in $CDCl_3$.



1: n = 3

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